Environmental Effects and Interactions of Stratospheric Ozone Depletion, UV Radiation, and Climate Change

2018 Assessment Report

Montreal Protocol on Substances that Deplete the Ozone Layer

UN environment
United Nations Environment Programme
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Contributions of the Montreal Protocol to a Sustainable Earth

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Introduction

This Quadrennial Assessment was prepared by the Environmental Effects Assessment Panel (EEAP) for the Parties to the Montreal Protocol. The Assessment reports on key findings on environment and health since the last full Assessment of 2014, paying attention to the interactions between ozone depletion and climate change. The assessment is produced in the first instance as a limited edition for governments of all countries, via the United Nations Environment Programme (UNEP), and is made more readily available to the scientific community by publication in the scientific literature. The 2018 Assessment will be published in the journal, Photochemical & Photobiological Sciences, **18**, 2019.

This ninth Quadrennial Assessment represents the work of forty-two members and co-authors of the Environmental Effects Assessment Panel from 18 countries. Our assessment considers the interactive effects of ozone depletion, anticipated ozone recovery, and climate change on human health and the environment, especially effects mediated via changes in UV radiation reaching the Earth's surface. The assessment highlights the contribution of the Montreal Protocol to environmental sustainability, human health and well-being, and the alignment with many of the UN Sustainable Development Goals. The Montreal Protocol and its Amendments, through controlling the ozone depleting substances over the past 34 years, has helped to avoid large increases of solar UV-B (280–315 nm) radiation that would otherwise have occurred by the middle of the 21st century. Modelling studies of a world without successful control of ozone depleting substances, the so-called 'world avoided', show that implementation of the Montreal Protocol and its Amendments has prevented catastrophic effects on human health. Globally, the implementation of the Montreal Protocol has protected crop production from the damaging effects of both elevated UV radiation and climate change. However, to date, there are no 'world avoided' models of these effects on the environment. As editors and Panel members, we hope this report will help keep scientists aware of their involvement in the protection of the environment for all forms of life on Earth.

Janet F. Bornman, Nigel Paul, Min Shao

Co-Chairs of the Environmental Effects Assessment Panel

Acknowledgments

This assessment would not have been possible without the contributions of the reviewers (names and addresses listed on pages 378–382), all of whom made written and/or verbal comments on the content of the Chapters in this assessment. We thank them for their generous contribution of time and knowledge.

Review meeting

The review meeting of the Panel was held in Essex, Vermont, USA. We thank staff of *The Essex* for their hospitality and for making our stay very enjoyable as well as productive.

Support for participation in the activities of the Panel

The UNEP Ozone Secretariat funds participation of members of the Environmental Effects Assessment Panel from developing countries and provided funds for the participation of four reviewers from developing countries. Acknowledgments for the participation of other Panel Members and Co-Authors are provided at the end of each chapter.

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Executive Summary

Environmental Effects Assessment Panel

2018 Quadrennial Assessment on the Environmental Effects and Interactions of Stratospheric Ozone Depletion, UV Radiation, and Climate Change: Contributions of the Montreal Protocol to a Sustainable Earth

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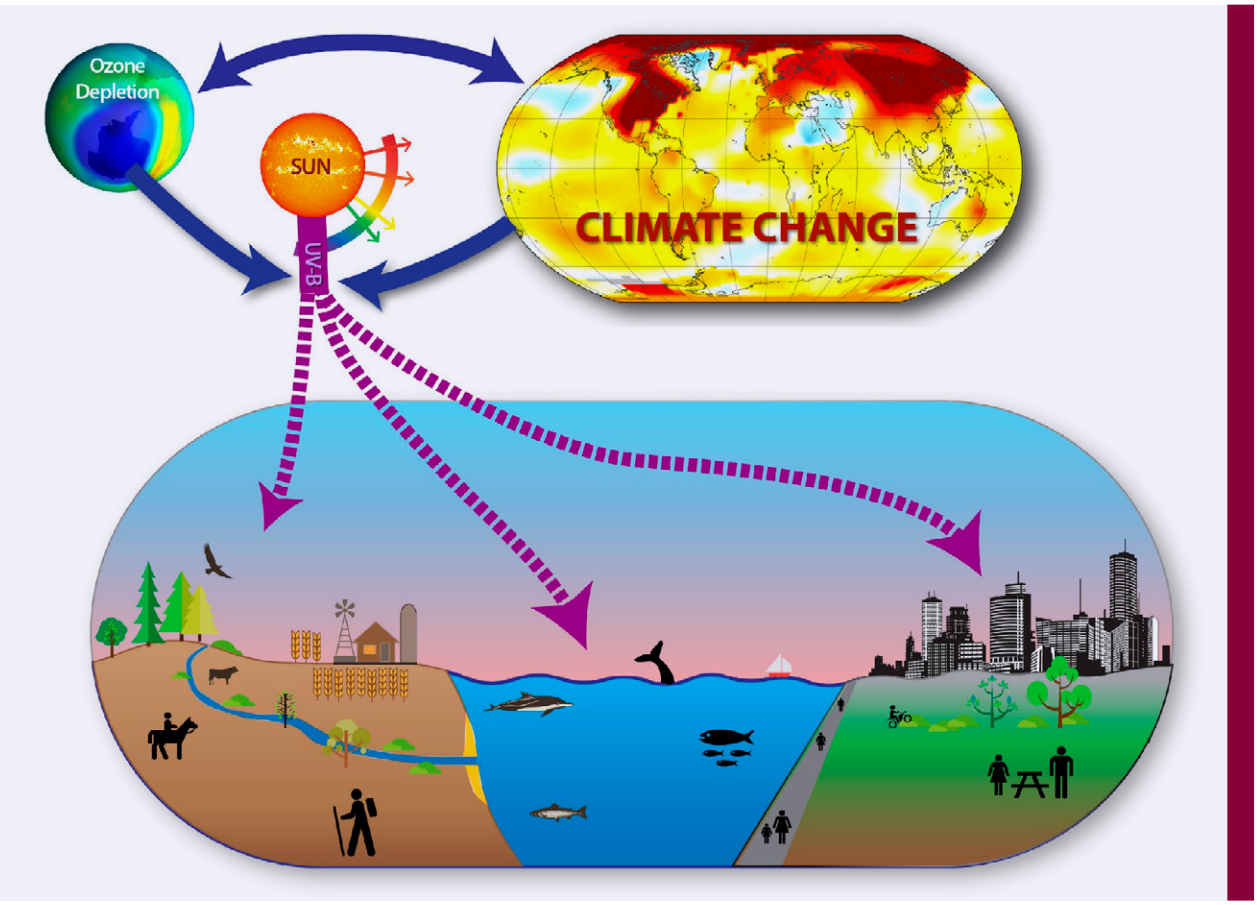


Fig. 1 **Linkages between the effects of depletion of stratospheric ozone, climate change, and implications for environment and human health.**

Stratospheric ozone depletion, the Montreal Protocol, and the Environmental Effects Assessment Panel

Thirty-four years ago, an unprecedented thinning of stratospheric ozone was reported over Antarctica.[21] The risk of a consequent increase in exposure to solar UV-B radiation (UV-B; wavelengths 280–315 nm) raised concerns about potentially disastrous effects on human health and the Earth's environment. In response, the international community mobilised and worked together to understand the causes and find a solution to this dramatic change in the Earth's atmosphere. In 1985, the Vienna Convention for the Protection of the Ozone Layer was signed, which provided the framework for the *Montreal Protocol on Substances that Deplete the Ozone Layer,* signed in 1987. In these international agreements, the United Nations recognised the fundamental importance of stopping and reversing ozone depletion and preventing its damaging effects. The Montreal Protocol, with its subsequent Amendments and Adjustments, was negotiated to control the consumption and production of anthropogenic ozone-depleting substances. The Parties to the Montreal Protocol base their decisions on scientific, environmental, technical, and economic information provided by three Assessment Panels (Box 1).

Box 1 The Environmental Effects Assessment Panel

The Environmental Effects Assessment Panel is one of the three Assessment Panels established by the Montreal Protocol to assess various aspects of stratospheric ozone depletion. These three Panels have complementary charges. The Scientific Assessment Panel assesses the status of the depletion of the ozone layer and relevant atmospheric science issues. The Technology and Economic Assessment Panel provides technical and economic information on alternative technologies to replace ozone depleting substances. The Environmental Effects Assessment Panel (EEAP) assesses the full range of potential effects of stratospheric ozone depletion, in conjunction with climate change, on UV radiation at the Earth's surface and consequent effects on human health, aquatic and terrestrial ecosystems, biogeochemical (e.g., carbon, nitrogen, metals, contaminants) cycles, air quality, and materials for construction and other uses. Forty-three scientists from eighteen countries contributed to the 2018 EEAP Quadrennial Assessment.

The implementation of the Montreal Protocol has successfully prevented the global depletion of the stratospheric ozone layer.[94] Concentrations of ozone depleting substances have been declining in the stratosphere since the late 1990s. While significant seasonal ozone depletion over Antarctica has occurred annually since the 1980s (called the "ozone hole"), there have been small, but significant, trends toward higher amounts of total column ozone in Antarctica in spring over the period 2001–2013. Global mean total ozone has been projected to recover to pre-1980s levels by about the middle of the 21st century, assuming full compliance to the Montreal Protocol.[94]

Many of the chemical compounds controlled by the Montreal Protocol are not only ozone depleting substances but also potent greenhouse gases.[53] Modeling studies indicate that, in the absence of the Montreal Protocol, global mean temperatures would have risen by more than 2°C by 2070, due to the warming effects from ozone-depleting substances alone.[25] Furthermore, the adoption of the Kigali Amendment to the Montreal Protocol in 2016 limits

the production and consumption of hydrofluorocarbons, powerful greenhouse gases that are used as substitutes to ozone-depleting substances.[64] This amendment has further broadened and strengthened the scope of the Montreal Protocol, creating an effective international treaty that not only addresses stratospheric ozone depletion, but is doing more to protect global climate than any other human actions to date.[11, 60, 83, 96]

Box 2 The United Nations Sustainable Development Goals (SDGs) addressed by the 2018 Quadrennial Assessment of the Environmental Effects Assessment Panel

Our findings address the following UN Sustainable Development Goals (SDG):
2. **Zero hunger,** 3. **Good health and well-being,** 6. **Clean water and sanitation,** 7. **Affordable and clean energy,** 9. I**ndustry, innovation and infrastructure,** 11. **Sustainable cities and communities,** 12. **Responsible consumption and production,** 13. **Climate action,** 14. **Life below water,** 15. **Life on land.** More information on these SDGs can be found at: https://www.un.org/sustainabledevelopment/sustainable-development-goals/

One of the important reasons for the success of the Montreal Protocol has been its foundation on high quality science, which not only improves our understanding of the causes and mechanisms of ozone depletion, but also of the potential environmental effects of these atmospheric changes. The Environmental Effects Assessment Panel (EEAP) is specifically charged with providing assessments of the state of the science on the environmental effects

of ozone depletion and consequent changes in UV radiation as well as interactions with global climate change (Box 1). Because of the direct involvement of the Montreal Protocol in mitigating climate change, as well as the strong physical and biological linkages that exist between the effects of stratospheric ozone depletion and climate change, the Environmental Effects Assessment Panel necessarily addresses the consequences of ozone depletion in the context of a changing global climate.

This Executive Summary presents key findings from the most recent EEAP Quadrennial Assessment and considers the significant societal implications of environmental effects. The multiple ways by which the Montreal Protocol is contributing to environmental sustainability and human health and well-being are highlighted, together with their contribution to, and consistency with, many of the United Nations Sustainable Development Goals (Box 2).

In-depth information on stratospheric ozone depletion and its environmental effects can be found in the full Assessments published by the Ozone Secretariat of the United Nations Environment Programme (https://ozone.unep.org) and elsewhere (Photochemical & Photobiological Sciences journal).[2, 6, 10, 46, 75, 90, 93] By focusing on the interacting effects of stratospheric ozone dynamics, UV radiation, and climate change, the report from the Environmental Effects Assessment Panel complements that of the Intergovernmental Panel on Climate Change (https://www.ipcc.ch; summarised in ref.[59]) to provide a comprehensive assessment of the environmental effects of these global changes in the Earth's atmosphere.

Key Findings and Highlights

1 Stratospheric ozone, climate change, and UV radiation at the Earth's surface

Depletion of stratospheric ozone leads to increased UV-B radiation at the Earth's surface (Chapter 1). However, because of the success of the Montreal Protocol,[94] present-day increases in UV-B radiation due to stratospheric ozone depletion have been negligible in the tropics, small (5–10%) at mid-latitudes (30–60°), and large only in polar regions. With the predicted recovery of stratospheric ozone over the next several decades, the clear-sky noontime UV Index[1] is expected to decrease at all latitudes outside the tropics, with the greatest decreases over Antarctica (Chapter 1 and refs[6, 52]). New projections of the UV Index for the end of the 21st century relative to the current decade suggest a decrease by 35% over Antarctica, and up to 6% over mid-latitudes (Chapter 1 and refs[6, 52]). These future projections are, however, uncertain because stratospheric ozone levels will be controlled not only by decreasing ozone depleting substances, but also by climate change due to increases in greenhouse gases for the rest of the 21st century.

Future changes in surface solar UV radiation of all wavelengths will depend on changes in clouds, aerosols, and surface reflectivity (e.g., from snow and ice cover) (**Fig. 2**). Climate change is altering cloud cover, with some regions becoming cloudier and others less cloudy.[73] Increased cloud cover generally tends to reduce UV radiation at the Earth's surface, but effects vary, for example, with the type of clouds.[40] Aerosols (solid and liquid particles suspended in the atmosphere (Chapter 6) reduce and scatter UV radiation. The type and amounts of aerosols in the atmosphere are affected by the emissions of air pollutants, volcanic activity, as well as the frequency and extent of wildfires and dust storms, and many other factors that are being affected by climate change (Chapters 1, 5, and refs[6, 75, 91]). In heavily polluted areas (e.g., in southern and eastern Asia), expected improvements in air quality are predicted to result in levels of UV radiation increasing towards pre-industrial levels (i.e., before the occurrence of extensive aerosol pollution), with the extent of changes contingent on curtailing the emissions of air pollutants.

High surface reflectance from snow or ice cover can enhance incident surface UV radiation because some of the reflected UV radiation is scattered back to the surface by air molecules, aerosols, and clouds in the atmosphere.[35] However, climate change-driven reductions in ice or snow cover in polar regions and mountains reduce the reflection of UV radiation from the Earth's surface and thus may reduce above-ground UV radiation in these regions (Chapter 1).

1 UV Index is an international standard measure of the strength of sunburn-producing UV radiation at a particular place and time.

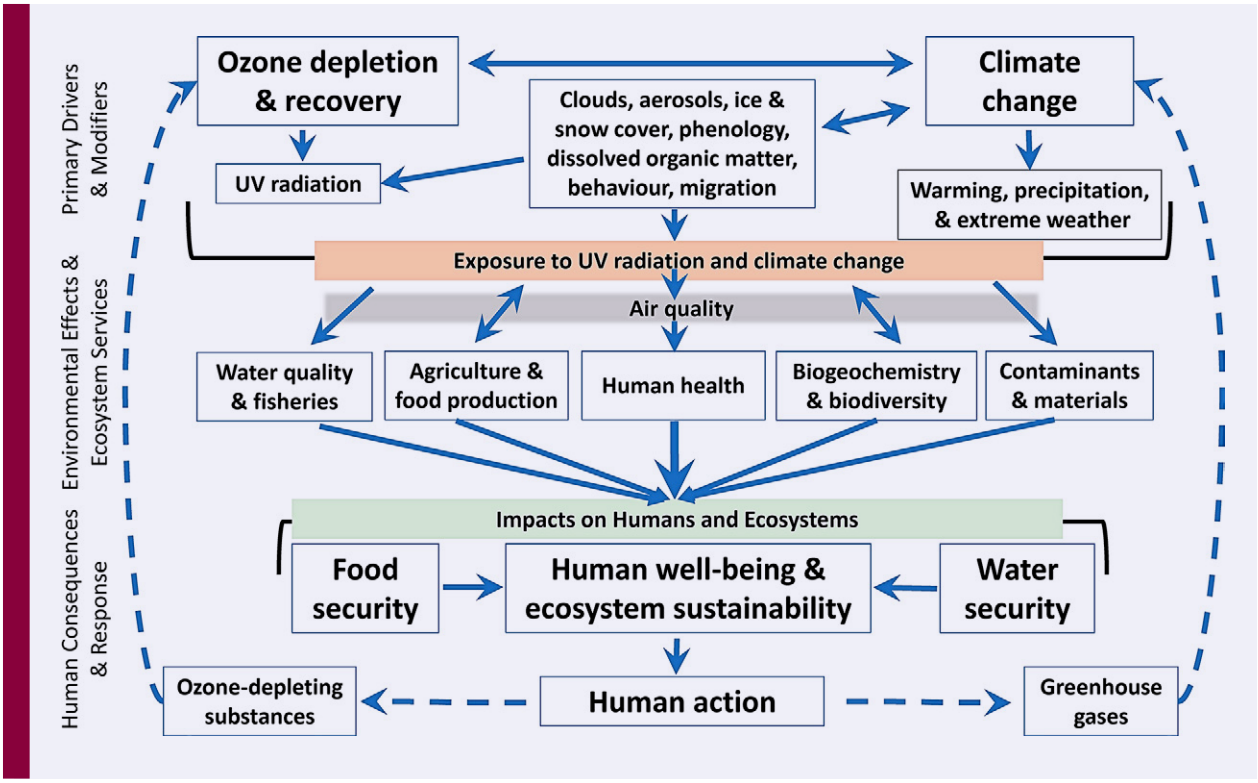


Fig. 2 **Linkages between stratospheric ozone depletion, UV radiation, and climate change, including environmental effects and potential consequences for human well-being, food and water security, and the sustainability of ecosystems (solid lines), with important feedback effects driven by human action (double-arrow solid lines) and other processes (dashed lines).**

1.1 Exposure to UV radiation and effects of climate change on exposure

The effect of UV radiation on organisms (including humans), natural organic matter, contaminants and materials depends on their exposure to the radiation (**Fig. 2**). This is determined by several factors besides stratospheric ozone depletion, including the effects of global climate change (Chapters 1 and 5, and refs[6, 75, 92]). Unlike stratospheric ozone depletion, these climate change-driven effects modify exposure not just to UV-B radiation but also to solar radiation in the ultraviolet-A (UV-A; 315–400 nm) and visible (400–700 nm) parts of the solar spectrum. These changes are important as many of the environmental and health effects caused by exposure to UV-B radiation are also influenced, to varying degrees, by UV-A and visible radiation (Chapters 2, 3, and 4).

For human health, behaviour is an important regulator of exposure to UV radiation. The exposure of individuals to UV radiation varies from one-tenth to ten times the average for the population,[26] depending on the time people spend indoors *vs* outdoors and under shade structures. The exposure of the skin or eyes further depends on the use of sun protection such as clothing or sunglasses. Warming temperatures and changing precipitation as a result of climate change will alter human behaviours in relation to sun exposure,[95] but the direction and magnitude of effect is likely to be highly variable across the globe. The dose

of UV radiation to biological structures in the skin is mediated by skin pigmentation, with darker skin providing significant protection against skin cancers. If humans are displaced, for example, due to climate-change induced sea-level rise,[70] (e.g., darker-skinned people moving from low to higher latitudes) they will encounter conditions of UV radiation that may be different to those to which they are accustomed.

Vegetation cover modifies the amount of sunlight reaching many terrestrial organisms e.g.,[63] and shading influences the exposure of construction materials to UV radiation. Modifications of that cover, for example, as a result of drought, fire, and pest-induced die-back of forest canopies induced by climate change will have profound effects on the exposure of terrestrial organisms to UV radiation.e.g.,[63] In addition, shifts in the seasonal timing of critical life cycle events such as plant flowering, spring bud-burst in trees, and animal emergence and breeding[15, 22, 77] will change exposure to UV radiation as UV radiation naturally varies with season.

As plants and animals move poleward,[22] into higher elevations,[72] or deeper into lakes, and oceans[81] in response to climate change, they are exposed to conditions of UV radiation that may be different to those to which they are adapted. Furthermore, reductions in ice or snow cover in polar regions as a result of global warming will increase the exposure to UV radiation of soils and aquatic ecosystems that would previously have been below the snow or ice.[35]

The penetration of UV radiation into aquatic ecosystems depends on the transparency of water, the amount of dissolved organic matter, and ice cover.[89, 91] Increases in extreme weather events that increase the input of dissolved organic matter and sediments into coastal and inland waters can reduce water clarity, reducing exposure of aquatic ecosystems to UV radiation.[89, 91] Reductions in the thickness and duration of snow and ice cover and global changes in the depth of the warmer, surface mixed layers of lakes and oceans, are altering the levels of exposure of aquatic organisms to UV radiation (Chapter 4). Previously, climate change was expected to increase exposure to UV radiation by causing shallower mixed layers, but new data show deeper mixed layers in lakes and oceans in some regions and shallower mixed layers in others (Chapter 4).

These climate change-driven effects can result in either increases or decreases in exposures to solar UV radiation, depending on location, time of year, individual species, and other circumstances. Changes in exposure and sensitivity to solar UV radiation, driven by ongoing changes in stratospheric ozone and climate, have the potential to affect humans, life on Earth and the environment, including materials used in infrastructure and for other purposes, with consequences for the health and well-being of people and ecosystem sustainability. Some of these effects are highlighted below. These findings, together with others described in the current Quadrennial Assessment of 2018, address 11 of the 17 United Nations Sustainable Development Goals (Box 2).

2 Consequences of changing exposure to UV radiation on humans and the environment

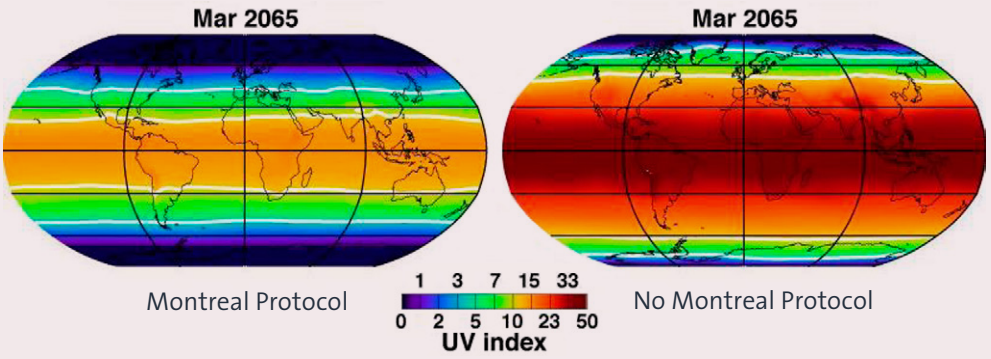
2.1 Effects on human health

Higher exposure to UV radiation increases the incidence of skin cancers and other UV-induced human diseases, such as cataracts and photosensitivity disorders (Chapter 2). Increases in the incidence of skin cancer over the last century appear largely attributable to changes in behaviour that increase exposure to UV radiation; these changes highlight how susceptible human populations are to higher exposure to UV radiation, as would have occurred with uncontrolled depletion of stratospheric ozone. Skin cancer is the most common cancer in many developed countries with predominantly light-skinned populations (Chapter 2). For example, there are over 90,000 new skin cancers compared with ca 3000 new cases of colorectal cancer in New Zealand each year. Skin cancer is also the most expensive cancer in many of these countries (Chapter 2). The estimated cost of treating cutaneous malignant melanoma in the USA was estimated at ca USD 457 million in 2011 and predicted to increase to ca USD 1.6 billion in 2030.[28] Exposure to UV radiation accounts for 60–96% of the risk of developing cutaneous malignant melanoma in light-skinned populations. It is estimated that ca 168,000 new melanomas in 2012 were attributable to 'excess' exposure to UV radiation (above that of a historical population with minimal exposure), as a result of population changes in lifestyle, from sun avoidance to sun-seeking behaviour.[4] Modelling studies show that implementation of the Montreal Protocol has avoided devastating effects on human health, including large increases in skin cancer incidence in light-skinned populations, resulting from high levels of UV radiation (e.g., UVI > 40 in the tropics by 2065.[54]) (Box 3).

Box 3 Environmental effects in the 'world avoided'

This assessment focusses largely on the environmental effects of changes in stratospheric ozone that have occurred, and are predicted to occur, due to the effective implementation of the Montreal Protocol and its Amendments. At present, lack of relevant research has prevented us from more fully assessing the health and environmental impacts that would have resulted if the stratospheric ozone layer had not been protected by actions of the Montreal protocol. However, it is worth noting that current understanding of this 'world avoided', provides the context for the effects observed with the successful implementation of the Montreal Protocol.

Several modelling studies reported changes in the stratospheric ozone layer that would have occurred without the Montreal Protocol, i.e., in a 'world avoided' scenario (for example,[55]). All point to progressive loss of stratospheric ozone that would have accelerated over time and extended to affect the entire planet by the second half of this century. This collapse in global stratospheric ozone would have resulted in UV Index values above the current extreme of 25 becoming common-place over almost all inhabited areas of the planet, and as high as 40 in the tropics, nearly five times the UV Index that is currently considered 'extreme' by the World Health Organization. Illustrated below is the comparison of the predicted UV Index (UVI; left) with that of the 'world avoided' (right) (from ref.[54]).



Combining these models of stratospheric ozone and UV radiation with understanding of the links between exposure to excessive UV radiation and the risk of skin cancers has allowed some quantitative estimates of the incidence of skin cancer in the 'world avoided'. Although different studies have considered different time-scales and/or different geographical regions, the successful implementation of the Montreal Protocol has prevented many millions of cases of skin cancers. For example, a report by the United States Environment Protection Agency,[82] showed that when compared with a situation of no policy controls, full implementation of the Montreal Protocol and its Amendments has avoided more than 250 million cases of skin cancer in the USA alone. The same report estimates that the Montreal Protocol will have prevented more than 45 million cases of cataracts in the USA. Substantial gaps in our knowledge currently limit our ability to quantitatively assess the full range of human and environmental benefits of the successful implementation of the Montreal Protocol.

Exposure to UV radiation contributes to the development of cataract, the leading cause of vision impairment globally (12.6 million blind and 52.6 million visually impaired due to cataract in 2015).[23] Particularly in low-income countries – often with high ambient UV radiation – access to cataract surgery may be limited, making this not only a major health concern but a major source of loss of livelihood and economic damage. The role of exposure to UV *vs* visible radiation in age-related macular degeneration remains unclear. Nevertheless, in aging populations worldwide, this is a major cause of visual impairment that currently has limited treatment options. Understanding risk factors and thus potential prevention is of critical importance (Chapter 2).

Concern about high levels of UV-B radiation because of stratospheric ozone depletion was an important driver for the development of programs for sun protection in many countries. These programs focus on promoting changes in people's behaviour, supported by structural and policy-level interventions.[68] Sun protection programs have been shown to be highly cost-effective in preventing skin cancers.[27] Behavioural strategies need to be informed by the real-time level of ambient UV radiation (provided by the UVI) and include controlling time outdoors together with using clothing, hats, sunscreen and sunglasses to reduce exposure to UV radiation. Behavioural changes can be facilitated by providing shade in public spaces such as parks, swimming pools, and schools, and improving access to sunscreen.[68]

Exposure to UV radiation also has benefits for human health. For example, exposure of the skin to UV radiation results in the production of vitamin D and is the major source of this vitamin for much of the world's population. Vitamin D is critical to healthy bones, particularly

during infancy and childhood. There is also growing evidence of a range of other benefits of exposure to UV radiation through both vitamin D and non-vitamin D pathways; for example, for systemic autoimmune diseases (such as multiple sclerosis),[45] in the prevention of myopia (short sightedness; Chapter 2), and reducing non-cancer mortality.[43] Recent research suggests that the benefits for reduced mortality may be substantial.[44]

Gaps in our knowledge prevent calculations of the amount of UV radiation necessary to balance the risks with benefits, particularly as this likely varies according to age, sex, skin type, and location. Projected changes in climate will alter the balance of risks *vs* benefits for human populations living in different regions. For example, lower ambient UV-B radiation at high latitudes will increase the risk of vitamin D deficiency where this risk is already substantial. Conversely, warmer temperatures may encourage people in cooler regions to spend more time outdoors, increasing exposure to not just UV-B radiation, but all wavelengths of solar radiation, and related risks of skin cancer and cataract (Chapter 2).

2.2 Effects on air quality

UV radiation drives photochemical reactions of many emitted chemical compounds, generating secondary pollutants, including ground-level ozone and some types of particulate pollutants. Future recovery of stratospheric ozone and climate may change ground-level ozone via decreases in UV radiation and increases in downward transport of stratospheric ozone (Chapter 6), with important consequences for human health and the environment. Modelling studies for the USA indicate that reductions in UV radiation due to stratospheric ozone recovery will lead to decreased ground-level ozone in some urban areas but slight increases elsewhere.[30]

Changes in UV radiation and climate can have major impacts on human health by affecting air quality (Chapter 6). A number of recent international assessments have concluded that poor air quality is a significant global health issue and is estimated to be the largest cause of deaths globally due to an environmental factor; for example, exposure to fine particulate matter ($PM_{2.5}$) caused 4.2 million deaths in 2015.[14] Because large populations are already affected by poor air quality, even small relative changes in UV radiation can have significant consequences for public health.

2.3 Effects on agriculture and food production

There is little evidence to suggest that modest increases in solar UV radiation have any substantial negative effect on crop yield and plant productivity (Chapter 3). How food production would have been impacted by large increases in solar UV radiation in the absence of the Montreal Protocol is unclear. One analysis, based on data from a number of field studies conducted in regions where stratospheric ozone depletion is most pronounced (i.e., high latitudes), concluded that a 20% increase in UV radiation equivalent to a 10% reduction in stratospheric ozone would reduce plant production by only about 6% (i.e., a 1% reduction in growth for every 3% increase in UV radiation).[7] To what extent this relationship would hold for levels of UV radiation > 2-fold higher than present (i.e., the "world avoided" scenario (Box 3)) is uncertain and represents an important knowledge gap.

It is likely that by contributing to the mitigation of climate change through phasing out of the ozone depleting substances and some of their substitutes that increase global warming, the Montreal Protocol has reduced the vulnerability of agricultural crops to rising temperatures, drought, and extreme weather events.[3] It is now clear that ozone depletion in the southern hemisphere is altering regional atmospheric circulation patterns in this part of the globe[94] which, in turn, affect weather conditions, sea surface temperatures, ocean currents, and the frequency of wildfires.[13, 31, 38, 41, 58] At a regional scale, increases in rainfall in the southern hemisphere, driven by stratospheric ozone depletion and climate change, have been linked to increases in agricultural productivity in South America (Box 4); however, these beneficial effects may reverse as the stratospheric ozone 'hole' recovers. In the northern hemisphere, similar, but smaller, effects of stratospheric ozone depletion on climate may be occurring (Chapter 1), but there are no reports as yet linking these changes to environmental effects.

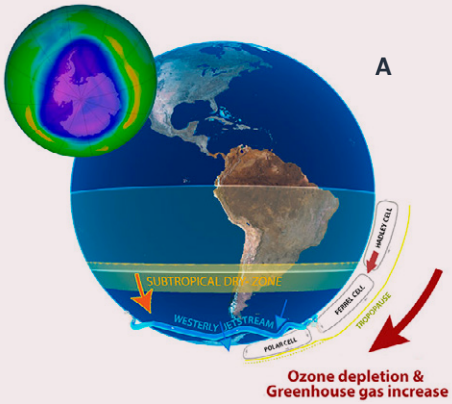
Climate change factors including drought, high temperatures, and rising carbon dioxide levels can modify how UV radiation affects crop plants, but effects are complex and often contingent on growth conditions. In some cases these factors can increase sensitivity to UV radiation (e.g., elevated carbon dioxide can weaken defenses against UV radiation in maize.[87] In other cases, exposure to UV radiation can alter the effects of climate change, such as increasing the tolerances of crop plants to drought.[67] Reduced UV radiation resulting from the recovery of stratospheric ozone may lead to increases in ground-level ozone in rural areas that could negatively affect crop yields (Chapter 6). Understanding these, and other, UV-climate change interactions can inform growers and breeders as to relevant agricultural practices for maintaining crop yields in the face of evolving environmental change.

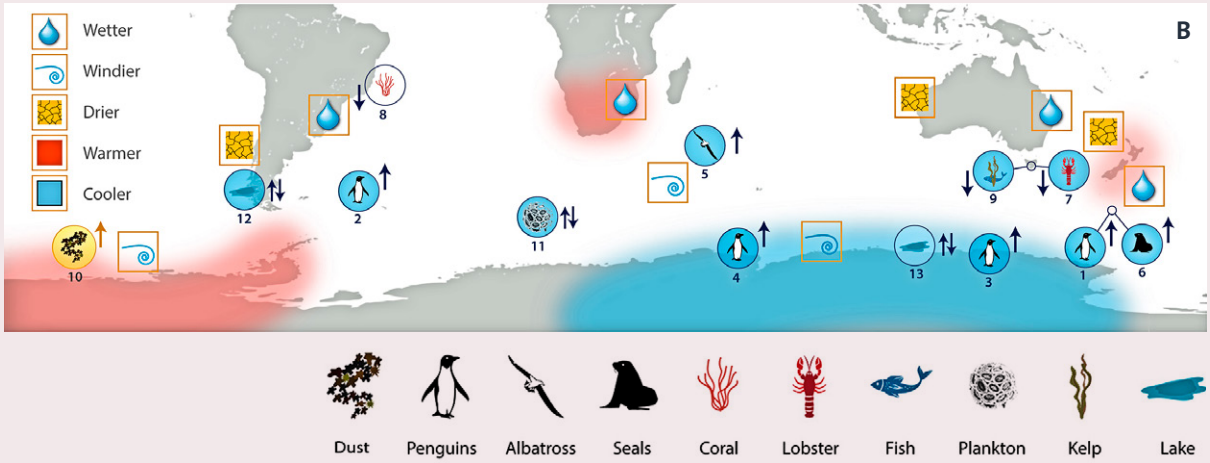
UV radiation can also have beneficial effects on plants and these effects are often mediated by specific photoreceptors that act to regulate plant growth and development.[34] These non-damaging effects include alterations in plant chemistry that then lead to changes in the nutritional quality of food[74] and plant resistance against pests and pathogens.[20] Consequently, decreases in exposure to UV radiation as a result of changes in stratospheric ozone and climate or changing agricultural practices (e.g., planting dates or sowing densities), may reduce plant defenses and thereby affect food security in ways other than just the direct effects on yield.[8] For certain vegetable crops, UV radiation is increasingly being used to manipulate plant hardiness, food quality and pest resistance.[85]

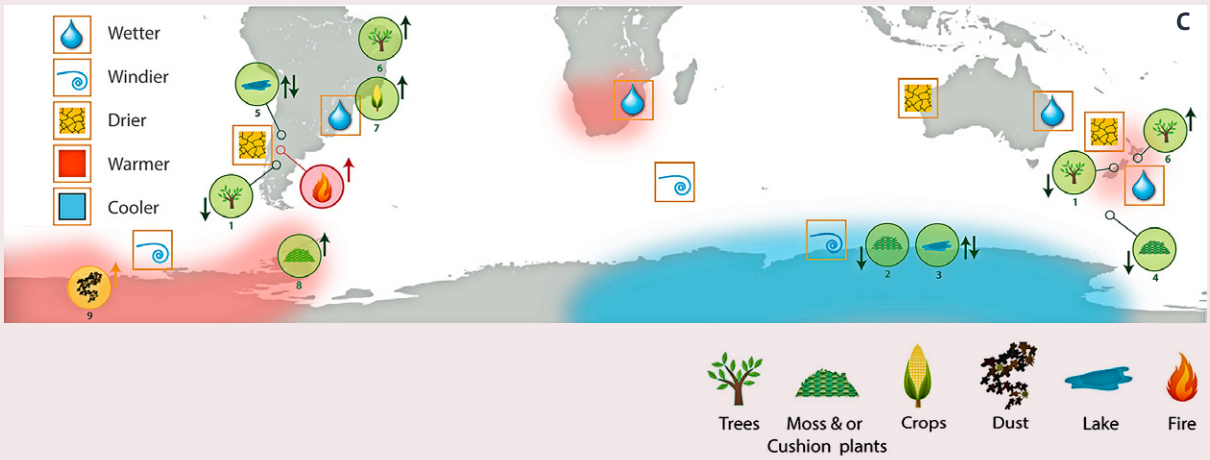
Box 4 Environmental effects of ozone-driven climate change in the southern hemisphere

Stratospheric ozone depletion and increases in greenhouse gases have both had measurable impacts on southern hemisphere climate, moving the winds and associated latitudinal bands of high and low rainfall further south (**A**). As a result, aquatic and terrestrial ecosystems, including agriculture, have been affected in several ways (**B**). For instance, the productivity of the Southern Ocean is changing, decreasing over much of the ocean, but increasing in other areas with corresponding changes in carbon dioxide uptake from the atmosphere.

On land, changing rainfall patterns have resulted in increased agricultural productivity in some regions and drought conditions in others (**C**). Drier conditions have resulted in increasing salinity in lakes and changed lake fauna in East Antarctica and the eastern Andes.







Arrows indicate direction of effects on biodiversity,
up = positive, down = negative effects, two-way arrows indicate changed biodiversity.

2.4 Effects on water quality and fisheries

Changes in exposure to UV radiation and mixing depths are altering the fundamental structure of aquatic ecosystems and consequently their ecosystem services (e.g., water quality, fisheries productivity) in regionally-specific ways. The larvae of many commercially important fish species are clear-bodied and sensitive to damage induced by UV radiation. This sensitivity, combined with the distribution of these larvae in surface waters with high exposure to UV radiation, has the potential to reduce the survival of first-year fish and subsequent harvest potential for fisheries.[32] In contrast, reductions in the transparency of clear-water lakes to UV radiation may increase the potential for invasions of UV-sensitive warm-water species that can negatively affect native species.[79]

Heavy precipitation and melting of glaciers and permafrost associated with climate change are increasing the concentration and colour of UV-absorbing dissolved organic matter and particulates (Chapters 4 and 5). This is leading to the "browning" of many inland and coastal waters, with consequent loss of the valuable ecosystem service in which solar UV radiation disinfects surface waters of parasites and pathogens.[89] Region-specific increases in the frequency and duration of droughts have the opposite effect, increasing water clarity and enhancing solar disinfection, as well as altering the depth distribution of plankton that provides critical food resources for fish.[81, 91]

2.5 Effects on biogeochemical cycles, climate system feedbacks, and biodiversity

Changes in stratospheric ozone and climate affect biogeochemical cycles driven by sunlight and, in turn, greenhouse gases and water quality. Exposure to solar UV and visible radiation can accelerate the decomposition of natural organic matter (NOM, e.g., terrestrial plant litter, aquatic detritus, and dissolved organic matter), and the transformation of contaminants (see section 2.6). Photodegradation of NOM results in the emission of greenhouse gases including carbon dioxide and nitrous oxide.[5, 17] Increases in droughts, wildfires, and thawing of permafrost soils driven by climate change have the potential to increase photodegradation (for example, ref. [1]), thereby fueling a positive feedback on global warming; however, the scale of this effect remains an important knowledge gap (Chapter 5).

Species of aquatic and terrestrial organisms differ in their tolerances to UV radiation and these differences can lead to alterations in the composition and diversity of ecological communities under conditions of elevated UV radiation (Chapters 3 and 4). UV radiation also modifies herbivory and predator-prey interactions, which then alter trophic interactions, energy transfer, and the food webs in ecosystems.[42] Presently, ozone-driven changes in regional climate in the southern hemisphere[3, 13, 31, 38, 39, 41, 58, 65] are threatening the habitat and survival of a number of species that grow in the unique high-elevation woodlands of the South American Altiplano[19] as well as for mosses and other plant communities in Antarctica,[66] but enhancing reproductive success of some marine birds and mammals (ref.[86], Box 4). To what extent the Montreal Protocol has specifically contributed to the maintenance of biodiversity in ecosystems is unknown, but losses in species diversity in aquatic ecosystems are known to be linked to high exposure to UV radiation and can cause declines in the health and stability of ecosystems and the services they provide to humans.[91]

2.6 Effects on contaminants and materials

Escalating releases of contaminants into the environment combined with changes in climate and stratospheric ozone impact human health and terrestrial and aquatic ecosystems. UV radiation is one of the key factors that influences the biogeochemical cycling of contaminants and their degradation via direct and indirect photoreactions. However, effects of climate change, such as heavy precipitation events or droughts also have large impacts on the photodegradation of contaminants by decreasing or increasing their exposure to solar UV radiation. Moreover, increased or decreased runoff of coloured dissolved organic matter affects the balance between direct and indirect photoreactions in aquatic ecosystems (Chapter 5). These effects of climate change depend on local conditions, posing challenges for prediction and management of contaminant effects on human health and the environment.

Exposure to UV-B radiation plays a critical role in altering the toxicity of contaminants (Chapters 4 and 5). Exposure to UV radiation increases the toxicity of contaminants such as pesticides and polycyclic aromatic hydrocarbons (PAHs) to aquatic organisms such as fish and amphibians. In contrast, exposure to UV-B radiation transforms the most toxic form of methylmercury to forms that are less toxic, reducing the accumulation of mercury in fish. However, potential long-term increases in dissolved organic matter will decrease underwater exposure to UV radiation in inland waters in some regions, such as southern Norway. This may then contribute to the already observed increases in methylmercury in fish that would likely occur as a consequence of reduced water transparency to UV radiation.[62] Solar radiation also plays a major role in the degradation of many organic pollutants and water-borne pathogens (Chapter 5). This process of photodegradation by solar UV radiation may be affected by changes in stratospheric ozone, but other factors such as dissolved organic matter are more important in regulating underwater UV radiation and so have a greater effect on photodegradation (Chapter 5). Advances in modeling approaches are allowing improved quantification of the effects of global changes on the fate of aquatic pollutants.

Sunscreens are in widespread use, including in cosmetics, as part of the suite of approaches to sun protection for humans. However, it is now recognised that sunscreens wash into coastal waters, with potential effects on aquatic ecosystems. The toxicity of artificial sunscreens to corals,[78] sea urchins,[16] fish,[24] and other aquatic organisms, has led the state of Hawaii, USA, to pass legislation banning the use of some sunscreens, and the European Union to consider similar legislation.[88]

Microplastics (plastic particles < 5mm) are now ubiquitous in the world's oceans and pose an emerging serious threat to marine ecosystems with many organisms now known to ingest them.[12] Microplastics are formed by the UV-induced degradation and breakdown of plastic products and rubbish exposed to sunlight. Microplastic pollutants occur in up to 20% or more of fish marketed globally for human consumption.[80] Although the toxicity of microplastics and smaller nanoplastics is unknown, higher temperatures and levels of UV radiation accelerate the fragmentation of plastics, potentially threatening food security.

Exposure to solar UV radiation damages the functional integrity and shortens the service lifetimes of organic materials used in construction, such as plastics and wood that are routinely exposed, e.g., in roofing and pipelines (Chapter 7). Until very recently, plastics used in packaging and building were selected and optimised on the basis of durability and performance (Chapter 7). However, the present focus on increased sustainability, for example, the trend towards 'green buildings', now requires such choices to be environmentally acceptable as well. This includes the increased use of wood, which is renewable, carbon-

neutral and low in embodied energy, in place of plastics, where appropriate. Some of these materials are vulnerable to accelerated aging under exposure to UV radiation. Current efforts are moving forward to identify and develop novel, safer, effective, and 'greener' additives (colourants, plasticisers, and stabilisers) for plastic materials and wood coatings. Harsher weathering climates, as predicted due to climate change, would require even more effort along this direction.

Trifluoracetic acid (TFA), a substance regulated under the Montreal Protocol, is produced naturally and commercially. There are multiple anthropogenic sources that will release trifluoroacetic acid (TFA) into the environment. Sources relevant to the Montreal Protocol include the substitutes for CFCs, the HCFCs, HFCs, and HFOs. These chemicals are known to degrade to TFA in the atmosphere (**Fig. 3**; Box 5) but contribute to only a slight increase in TFA concentrations in surface water. This is not expected to pose a risk to humans or the environment.[71]

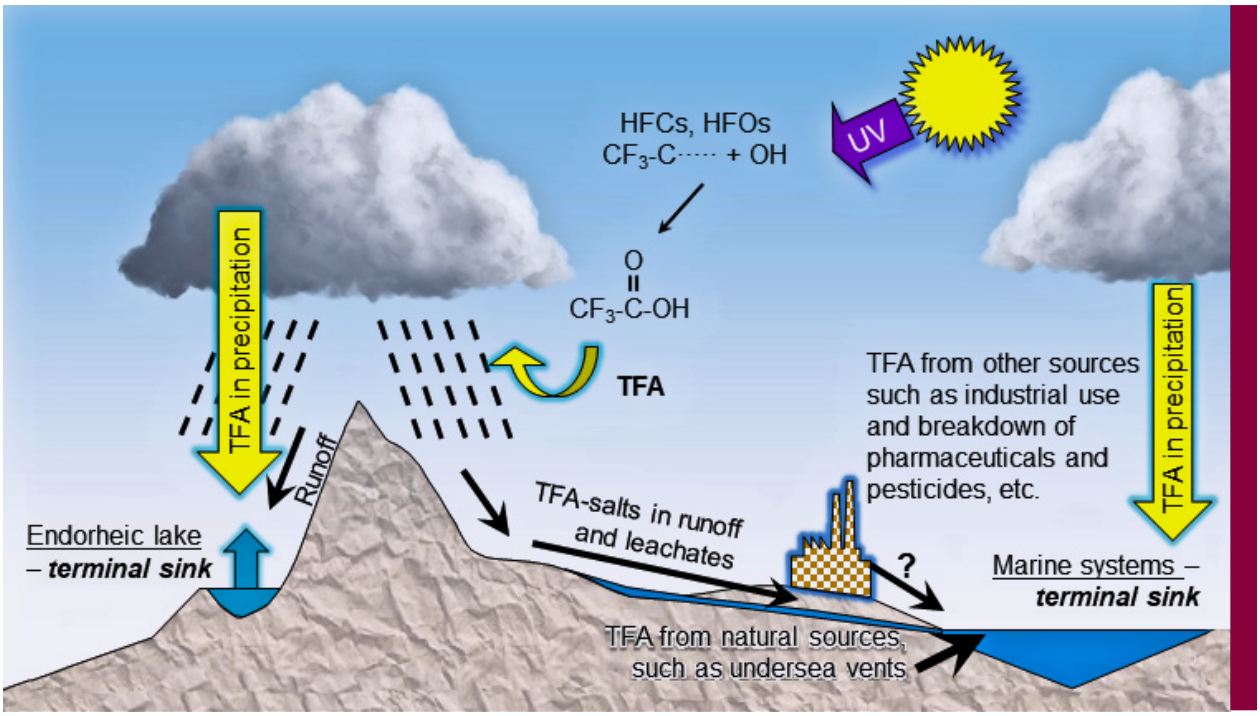


Fig. 3 **Trifluoracetic acid (TFA) formed from HFCs and HFOs in the atmosphere will rapidly partition from air to water in the atmosphere. It will combine with cations in soil and surface water and accumulate in endorheic water bodies (salt lakes) and the oceans (modified from ref.[71], with permission).**

Box 5 The environmental effects of replacements for ozone depleting substances

One of the advantages of chlorofluorocarbons (CFCs) was that they were inert in the lower atmosphere and had no direct impact on air quality. Their replacements have been specifically chosen to be less stable, and since these compounds are directly relevant to the implementation of the Montreal Protocol, their impacts on air and environmental quality need to be considered. Focusing on refrigeration, these replacements include hydrofluorocarbons (HFCs) and hydrofluoroolefins (HFOs), hydrocarbons and ammonia.

HFCs and HFOs

Trifluoracetic acid (TFA) is a persistent substance that is formed in the atmosphere from several HCFCs, HFCs, and HFOs. There are also many other sources of TFA in the environment, but since they are unregulated, there are virtually no data on global production and release to the environment.[69] HFCs degrade slowly in the atmosphere (1–100 years) and so become globally distributed. By contrast, HFO-1234yf degrades to TFA rapidly (days – weeks). As a result, breakdown will occur closer to the regions where HFO-1234yf is released. This potential results in localised, higher concentrations of TFA in surface waters than from HFCs.[36, 47, 84] Even so, there is no evidence to date to suggest that these local depositions of TFA will result in risks to the environment, especially when eventual dilution occurs in the oceans.

Estimates of production of TFA in China, the USA, and Europe[84] and assuming no dilution, would be several orders of magnitude less than the chronic "no observable effect concentration" (NOEC) of 10,000,000 ng L^{-1} for TFA-Na salt from a microcosm study.[29]

Overall, there is no new evidence that contradicts the conclusion of our previous Assessments that exposure to current and projected concentrations of salts of TFA in surface waters present a minimal risk to the health of humans and the environment. A recent review of this topic[56] reached a similar conclusion.

Hydrocarbons

The release of hydrocarbons (such as propane and n-butane) used as ODS replacements will add to the burden of hydrocarbons in the atmosphere, and potentially increase the concentration of ground-level ozone.

There are few estimates of the effects of emissions of hydrocarbon refrigerants on air quality in the refereed literature. One recent assessment for three cities in the USA[37] highlights current uncertainty, providing a "worst case" increase in tropospheric ozone of around 13 µg m^{-3}, but a realistic estimate of 0.3 µg m^{-3}. These figures compare with a current annual peak tropospheric ozone concentration greater than 120 µg m^{-3}(Chapter 6).

Ammonia

Ammonia in the atmosphere reacts with several compounds to produce aerosols and hence increase concentrations of particulate air pollutants ($PM_{2.5}$). However, full replacement of current emissions of CFCs, HCFCs, and HFCs by ammonia (estimated to total 170,000 tonnes per annum: G. Velders, personal. comm., Feb. 2018; (Chapter 6) is small compared to estimated annual ammonia emissions from agriculture (34,500,000 tonnes[9]), or from industrial and residential activities (8,500,000 tonnes[49]).

3 Conclusions and knowledge gaps

The Montreal Protocol has been successful in preventing the global depletion of stratospheric ozone and consequently large-scale increases in solar UV-B radiation and has therefore prevented major adverse impacts on human health and the environment (Box 3).

We remain confident in our qualitative predictions of the effects on human health and the environment that have been avoided largely because the Montreal Protocol has successfully controlled stratospheric ozone depletion. However, quantification of many of the benefits deriving from the success of the Montreal Protocol remains a major challenge, and the future trends in UV radiation exposure remain uncertain considering climate change and the extent of human response.

Unexpected increases in emissions of CFC-11 that were recently reported[51] are currently expected to have only small effects on stratospheric ozone depletion,[94] and therefore also on human health or the environment. However, were such unexpected emissions to persist and increase in the future, or new threats emerge, effects on human health and the environment could be substantial. New threats might include "geoengineering" activities proposed to combat the warming caused by greenhouse gases,[33] which could have consequences for UV radiation reaching the Earth's surface. In particular, proposals to inject sulfuric aerosols into the stratosphere to reduce solar radiation at the Earth's surface[18] would likely have important side effects for stratospheric ozone and UV radiation. Sulfate aerosols could accelerate stratospheric ozone loss if substantial amounts of ODSs remain in the atmosphere. The combined changes in absorption by ozone and scattering by sulfate would have spectrally complex consequences for the transmission of UV radiation to ground-level, and the ratio of direct to diffuse UV radiation would be systematically larger.[48, 57, 76]

Meeting the challenge of improved quantification of the environmental effects of future changes in stratospheric ozone requires addressing several significant gaps in current knowledge. First, we need a better understanding of the relative effectiveness of different wavelengths of solar radiation (i.e. the biological spectral weighting functions) in altering the fundamental responses of a diversity of organisms. This would allow better attribution of changes to exposure, specifically to UV-B radiation (and thus related to stratospheric ozone depletion), rather than to solar radiation more generally. Second, we need a better understanding of dose-response relationships across the breadth of effects on human health and the environment. Taken together, these would support improved scaling and modeling of the effects of stratospheric ozone depletion and climate change on living organisms and their ecosystems, and materials such as plastics, wood structures, and clothing.

As a result of shifting geographic ranges (including migration of humans and other species that is induced by climate change) and changes in seasonal timing of life-cycle events due to climate change, it is apparent that many organisms, including human populations, will experience different and interactive combinations of UV radiation and other environmental factors. These environmental changes will occur together with alterations in community structure,[61] which will then indirectly affect growth, reproduction, and survival. How humans and ecosystems respond to changes in UV radiation against this backdrop of simultaneous, multi-factor environmental change remains a major knowledge gap. Quantifying these effects is extremely challenging, where many of the outcomes are contingent on human behaviour and societal responses that are difficult to predict.

The focus of concern regarding elevated exposure to UV radiation has historically been on human health. Beyond the importance of terrestrial and aquatic ecosystems in providing critical 'ecosystem services' for human well-being, environmental sustainability and the maintenance of biodiversity are critical to maintaining a healthy planet.[50] The topics covered by the Environmental Effects Assessment Panel embrace some of the complexity and interrelatedness of our living planet, while the success of the Montreal Protocol demonstrates that globally united and successful action on complex environmental issues is possible.

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1 Ozone-climate interactions and effects on solar ultraviolet radiation

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Summary

This report assesses effects of stratospheric ozone depletion and anticipated ozone recovery on the intensity of ultraviolet (UV) radiation at the Earth's surface. Interactions between changes in ozone and changes in climate, as well as their effects on UV radiation, are also considered. These evaluations focus mainly on new knowledge gained from research conducted during the last four years. Furthermore, drivers of changes in UV radiation other than ozone are discussed and their relative importance is assessed. The most important of these factors, namely clouds, aerosols and surface reflectivity, are related to changes in climate, and some of their effects on short- and long-term variations of UV radiation have already been identified from measurements. Finally, projected future developments in stratospheric ozone, climate, and other factors affecting UV radiation have been used to estimate changes in solar UV radiation from the present to the end of the 21st century.

New instruments and methods have been assessed with respect to their ability to provide useful and accurate information for monitoring solar UV radiation at the Earth's surface and for determining relevant exposures of humans. Evidence since the last assessment reconfirms that systematic and accurate long-term measurements of UV radiation and stratospheric ozone are essential for assessing the effectiveness of the Montreal Protocol and its Amendments and adjustments. Finally, we have assessed aspects of UV radiation related to biological effects and human health, as well as implications for UV radiation from possible solar radiation management (geoengineering) methods to mitigate climate change.

Due to the successful implementation of the Montreal Protocol, concentrations of ozone depleting substances (ODSs) have been declining since the late 1990s. As a result, the downward trend of global ozone, which was observed in the 1980s and 1990s, has not continued into the present. However, ground- and space-based observations indicate that there has not yet been a statistically significant increase in global (60°S–60°N) column ozone. During the austral spring in Antarctica, significant positive trends in total column ozone of about 1.7% per year have been reported for the period 2001–2013. New emissions of CFC-11 (an ODS that was phased out by the Montreal protocol) have recently been reported over eastern Asia. These emissions may already have caused a delay of the projected recovery of stratospheric ozone, which was previously estimated to occur around the middle of the 21st century for global mean total ozone.

Statistically significant decreases in UV-B radiation consistent with stratospheric ozone recovery have not yet been detected because of the large variability in UV-B radiation caused by factors other than ozone. Variability of UV-B radiation in Antarctica remains very large, with near record high UV Indices (UVIs) observed at the South Pole in spring 2015 and well below average UVIs in spring of 2016 and 2017. The Arctic remains vulnerable to large decreases in total ozone and concomitant increases in UV-B irradiance whenever meteorological conditions lead to a cold lower stratosphere in late winter and early spring. Without the Montreal Protocol, UV-B radiation levels would by now exceed those in the mid-1990s by up to about 20%. However, because of the success of the Montreal Protocol, they have remained essentially unchanged over that period at pristine sites.

Continuing decreases in clouds and aerosols (rather than changes in ozone) after the mid-1990s have been the main contributors to positive trends of UV radiation reported at some northern mid-latitude sites. No significant changes in UV radiation have been reported at pristine mid-latitude sites or in the tropics since the mid-1990s.

As changes in total ozone over mid-latitudes have been generally small since the onset of ozone depletion, changes in the attenuation of UV-B radiation under cloud-free skies in most populated areas are mainly controlled by the concentrations of aerosols and the wavelength dependence of their optical properties. Over polluted areas, insufficient knowledge of the absorption properties of aerosols remains one of the largest uncertainties in estimating surface UV irradiance from space or for projecting future UV radiation levels.

Several independent satellite records indicate that changes in large-scale patterns of clouds have occurred between the 1980s and 2000s with consequences for UV radiation at the surface. Between 60°S and 60°N, observed changes in cloud patterns are consistent with simulations from climate models and indicate a poleward retreat of mid-latitude storm tracks, widespread reduction in cloudiness resulting in increases of UV radiation at the surface at mid-latitudes between about 30° and 50° of both hemispheres, and expansion of subtropical dry zones. The primary drivers of these changes are increasing concentrations of greenhouse gases (GHGs) and, for the southern hemisphere, the Antarctic ozone 'hole'. Over the Arctic, cloud cover increased rapidly during the last 20 years due to warming of the lower troposphere and large reduction of sea-ice-cover, which led to enhanced evaporation.

For the remainder of the 21st century, amounts of stratospheric ozone will be controlled by the continuing decreases in ODSs and increases in GHGs. As a result, total column ozone is expected to increase above its levels observed in the pre-ozone-depletion period (1964–1980) at mid-latitudes, which will lead to decreases in UV-B radiation.

A new projection of the global distribution of the noontime UVI for the end of the 21st century (average of 2085–2095) relative to the present decade (average of 2010–2020) has been developed based on recent projections of ozone, reflectivity, clouds, and aerosols obtained from the Chemistry-Climate Model Initiative (CCMI). Results suggest that:

(1) Ozone recovery due to decreasing ODSs and increasing GHGs, leads to decreases in UVI at all latitudes outside the tropics. Average decreases are greatest (35%) over Antarctica in October and range between 2 and 6% over mid-latitudes.

(2) Projected changes in cloudiness lead to small (less than 1%) average increases or decreases in UVI over the mid-latitudes and the tropics, and up to 3% decreases at high latitudes. These changes vary spatially by between –10 and 15%. The greatest effect of clouds is projected for the Arctic with decreases in UVI exceeding at some locations 18%.

(3) Reductions in reflectivity due to melting of sea ice or snow and shifting of the melting season lead to average decreases in UVI of 1–8% over the northern high latitudes and the Arctic and up to 2% over southern high latitudes and particularly around the Antarctic continent.

(4) The projected decreases in concentrations of aerosols over urban areas, mainly of the northern hemisphere, result in average increases in UVI of 4–5%. Over heavily industrialized regions in Asia, such as China and India, where reductions in the UVI due to air pollution are currently large, projected increases are greater, ranging between about 25% and 40%. Effects of projected changes in aerosols over most of the southern hemisphere are negligible.

The scenario specifying the change of GHGs over the 21st century that was selected for these projections (RCP 6.0) may not reflect the actual development over this period. Since GHGs have a large effect on future changes in ozone, cloud cover, and reflectivity (in the Arctic), these projections are inherently uncertain and depend greatly on policy choices such as the curbing of GHG emissions, the continued adherence to the Montreal Protocol and the curtailing of the emissions of air pollutants, which result in high aerosol concentrations.

1 Introduction

This Chapter focuses on effects of stratospheric ozone depletion, anticipated ozone recovery, and climate change on UV radiation reaching the Earth's surface, as well as effects of other geophysical variables that affect UV radiation (**Fig. 1**). Before discussing new scientific findings attained since the previous Quadrennial Assessment report, a brief overview of the status of science at that time is provided, and then the main new findings related to ozone and climate science are briefly discussed. This background information is essential for understanding variations of UV radiation and assessing the contributions of the different factors that UV radiation depends on.

1.1 State of science in the 2014 EEAP report

The previous EEAP Assessment[12] reported that the Montreal Protocol was vital in protecting the ozone layer by reducing ozone-depleting substances (ODSs). As a result, any increases

in UV radiation observed since the mid-1990s over northern mid-latitudes[2] remained small. Changes in UV radiation were predominantly caused by variability in cloudiness and aerosols rather than changes in ozone. At the time of the previous report, statistically significant decreases in UV-B radiation (280–315 nm) attributable to the beginning of ozone recovery had not been detected in any season and at any location. The absence of detectable trends was explained by the large natural variability of UV-B radiation resulting from the many factors that influence it and the lack of suitable UV data prior to the 1990s.

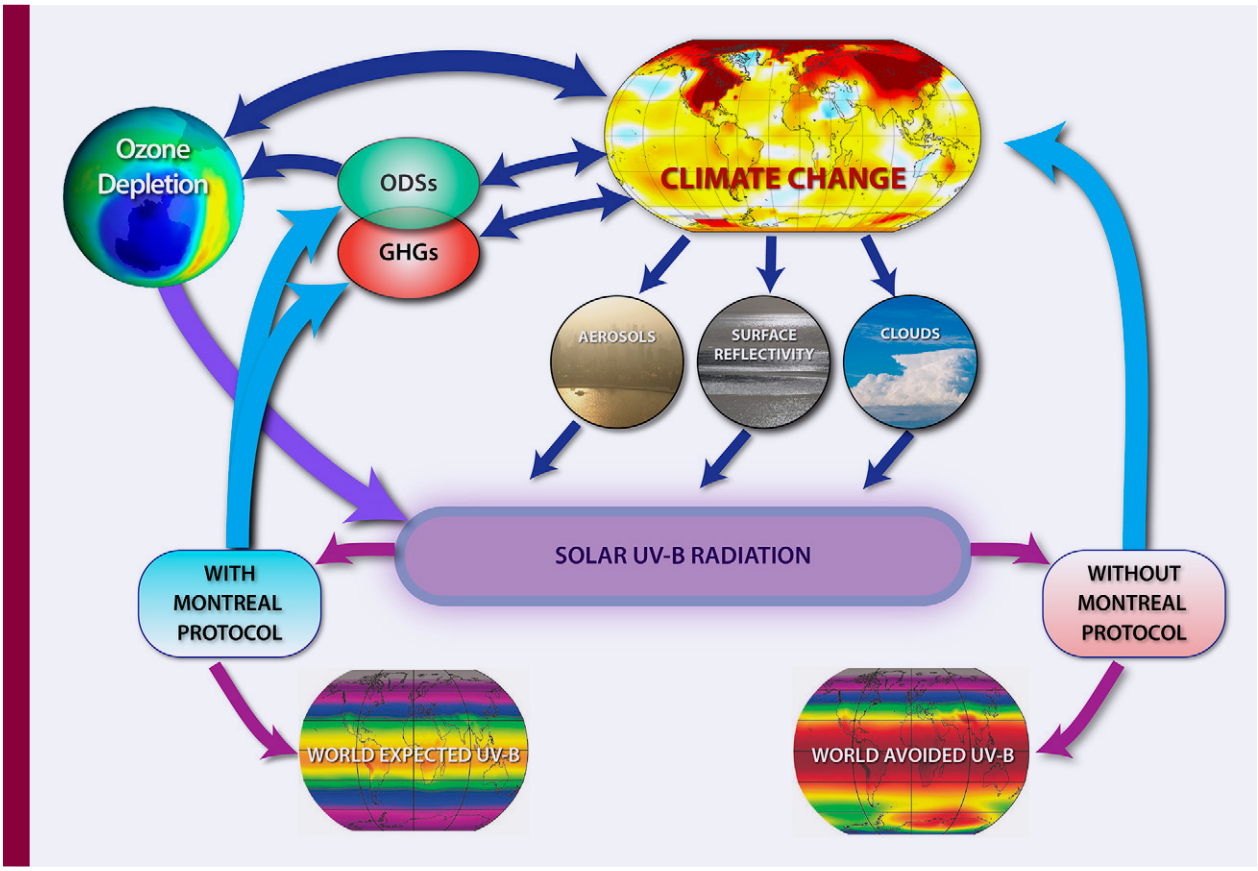

Fig. 1 **Conceptual representation of the interactive effects of changes in greenhouse gases (GHGs) and ozone-depleting substances (ODSs) on climate and solar UV-B radiation at the Earth's surface. Increases of ODSs in the atmosphere have led to stratospheric ozone depletion and the ozone 'hole'. Actions prompted by the Montreal Protocol has resulted in decreasing ODSs and has helped to avoid large increases of solar UV-B radiation that would otherwise have occurred by the middle of the 21st century. Continued emissions of GHGs (e.g., carbon dioxide, methane, and nitrous oxide) will change the climate and will also modify the recovery of stratospheric ozone, which is expected from decreasing concentrations of ODSs. Climate change will also affect clouds, surface reflectivity at high latitudes, where changes in sea ice and snow cover are expected, and aerosols near the Earth's surface. The combined effects of changes in ozone, aerosols, clouds, and reflectivity will determine future levels of UV-B radiation at the Earth's surface.**

2 Throughout this document the latitude ranges for both the northern and southern hemispheres are defined as: polar latitudes (80°–90°); high latitudes (60°–80°); mid latitudes (30°–60°); tropics (0°–30°).

Year-round increases in UV radiation were observed as early as the mid-1990s over some northern mid-latitude locations but were predominantly caused by reductions in cloudiness and aerosols. At several northern high-latitude sites, UV-B irradiance had decreased since the mid-1990s because of reduction in snow- and ice-cover. These decreases were most prominent in the summer and autumn. However, large, short-term increases in the erythemal (sunburning) UV dose had also been measured at several Arctic and Scandinavian sites in response to episodic decreases of stratospheric ozone, such as an event occurring in the spring of 2011[129] when the total erythemal UV dose accumulated over the low-ozone period of about 27 days increased by up to 50% at several sites in the Arctic and Scandinavia. Between February and April 2011, the total ozone at some locations was occasionally less than 50% of the climatological mean.

With continued effective implementation of the Montreal Protocol, future changes in UV-B irradiance outside the polar regions were projected to be dominated by changes in aerosols. These were projected to decrease significantly across the globe in the second half of the 21st century, particularly over heavily populated areas in Asia because of measures for improvement of air quality. However, confidence in the magnitude of the projected changes was low due to the uncertainty of future policies on emission controls.

Future levels of UV-B irradiance at high latitudes would be influenced by the recovery of stratospheric ozone and by changes in clouds and reflectivity of the Earth's surface. In Antarctica, reductions of up to 40% in noon-time erythemal UV radiation during spring were projected for 2100 because of the anticipated recovery of the stratospheric ozone. These projected reductions would be comparable in magnitude with the increases in UV radiation that had occurred in the past due to ozone depletion. Reductions in surface reflectivity due to ice-melt were projected to reduce UV-B irradiance by up to 10% in the Arctic, but confidence in the magnitude of these effects was low.

1.2 Current status of total and stratospheric ozone

The emissions and concentrations of ODSs in the atmosphere have been declining continuously since the mid-1990s because of the success of the Montreal Protocol. In response to this reduction in ODSs, global (60°S–60°N) column ozone is no longer declining. Small increases of 0.3 to 1.2% per decade since 1997 have been observed but are not statistically significant.[228] Different datasets of satellite and ground-based observations for the period 1997–2016 within 60°S–60°N show close to zero changes in total ozone for the tropics and the northern hemisphere (NH) and increases of 0.6% per decade for the southern hemisphere (SH). Generally, these changes are not statistically significant, except for two datasets showing small positive changes of 0.5 and 0.8% per decade in the tropics.[222] In recent years (2014–2017), total ozone has remained below the average of the 1964–1980 period: about 2.2% for the global average (60°S–60°N), about 3.0% for the northern mid-latitudes (35°N–60°N), about 5.0% for the southern mid-latitudes (35°S–60°S), and less than 1% for the tropics (20°S–20°N).[228] These estimates are essentially the same as those reported in the previous report of the Scientific Assessment Panel.[226] The only exception is Antarctica, where statistically significant increases in total ozone inside the polar vortex have now been observed for the period 2001–2013 in austral spring (about 1.7% per year, statistically significant at the 95% confidence level) and summer (about 0.5% per year, statistically significant at the 90% confidence level).[113, 195, 228] Further evidence of decreasing depletion of stratospheric ozone over Antarctica has been reported[202] by analyzing ozone and inorganic chlorine measurements for the period 2005–2016 using data from the Microwave Limb Sounder onboard the Aura satellite.

Analysis of ozone-profile data from nine stations in Antarctica[113] has confirmed results from an earlier study,[195] which reported the first signs of recovery of Antarctic ozone based on data from only two stations. Statistically significant (95% confidence level) positive trends in ozone concentrations for 2001–2013 were found in the lower stratosphere (altitude 10–20 km) for austral spring. Of note, the second study[195] omitted data from 2015, which was influenced by aerosols from the eruption of the Chilean volcano, Calbuco,[101, 201] and the long-lasting polar vortex,[150] both of which contributed to a record-sized ozone 'hole' that year. Subsequent studies have corroborated these conclusions with additional analyses of profiles from Antarctic ozonesondes[194] and multiple linear regression approaches with satellite data.[160]

There is some variation in trends in ozone measured at different altitudes and latitudes, and these are generally consistent with our understanding of the physics and chemistry of ozone.[44, 57] At mid-latitudes and the tropics, measured concentrations of ozone show an increase of 2–4% per decade in the upper stratosphere (altitude 35–45 km) since about 2000.[198] This increase is consistent with the projected recovery of stratospheric ozone resulting equally from decreasing concentrations of ODSs and increases in GHGs.[228] Increases of similar magnitude were also reported from combined data of different satellites for the period 1998–2016.[13] However, that same study found that ozone concentrations in the lower stratosphere (altitudes below 24 km) of tropical and mid-latitudes (60°S–60°N) continued declining by about 1.0% per decade in the same period. For total ozone, there were no statistically significant changes. These results were not able to be reproduced by state-of-the-art models used in that study,[13] but more recent model studies, extended to 2017, suggest that the apparent decrease in ozone in the tropical and mid-latitude lower stratosphere is the result of interannual variability in atmospheric circulation.[45, 200, 221] A longer record of observations is required to conclusively determine whether this trend in lower stratospheric ozone is a forced response to changes in ODSs or climate, or whether it is part of natural variability.

In the remainder of the 21st century, we expect that the amounts of stratospheric ozone will be controlled by continuing decreases in ODSs and increases in GHGs. Decreasing ODSs will lead to increases in the concentrations of ozone at all altitudes and latitudes. Increasing GHGs will lead to cooling of the upper stratosphere and to increasing concentrations of ozone in the upper stratosphere at all latitudes because the rate of ozone destruction is slower at lower temperatures. Moreover, increasing GHGs will lead to changes in circulation resulting in decreases in concentrations of ozone in the lower stratosphere at low latitudes. At mid latitudes, the effect in the lower stratosphere depends on the assumed GHGs emissions scenario.[34]

Generally, total ozone is expected to increase above its levels in the pre-ozone depletion period (1964–1980) at mid latitudes (termed "super recovery"), while in the tropics, total ozone will slightly decrease and remain below levels observed during the 1964–1980 period. These small decreases in tropical total ozone are driven by decreases in ozone in the lower stratosphere and their magnitude is dependent on GHG emissions.[57, 144]

In polar regions, cooling of the middle and upper stratosphere resulting from increased GHGs will drive increases in ozone in these atmospheric regions. For the lower stratosphere, the decline in ODSs will be the primary driver of increases in ozone over this century, with GHG-driven dynamical changes being additionally responsible for ozone increases in the Arctic (see also discussion in the following sections). However, the high interannual variability in stratospheric temperature in the Arctic means that individual years will likely continue to experience large losses of ozone throughout the 21st century.[228]

1.3 Benefits from the Montreal Protocol

1.3.1 Direct impacts

The implementation of the Montreal Protocol has already resulted in significant benefits for the stratospheric ozone layer and, consequently, for surface UV-B radiation. In the previous assessment, we discussed the direct environmental implications of the "world avoided" scenario, which describes a future without the Montreal Protocol where ozone depletion had continued unabated.[217] By 2070, increases in UV-B radiation would have led to peak UV Index (UVI)[3] values greater than 35 in the tropics and 5–15 at the sunlit northern polar cap, the latter being similar to or larger than the values found in the subtropics and tropics in 2000.[76] At mid latitudes, peak UVI values would have been approximately 3 times as high as in the period prior to the onset of ozone depletion.[153]

More recent calculations with a chemistry-transport model have shown that, without the Montreal Protocol, a deep Arctic ozone 'hole', with total ozone values below 120 Dobson Units (DU), instead of the usual 400–450 DU, would have occurred in 2011 given the meteorological conditions in that year.[46] The decline of stratospheric ozone over northern hemisphere mid-latitudes would also have continued, with depletion twice that actually experienced in 2013. In addition, the Antarctic ozone 'hole' would have been 40% larger in 2013 relative to the actual situation, with enhanced loss of ozone also at sub-polar latitudes of the SH. These large reductions in ozone since 1980 would have resulted in increases in springtime UV-B radiation at the Earth's surface of about 10% at mid-latitudes and over 20% at high latitudes of both hemispheres in 2013, with important implications for the health of humans (Chapter 2) and ecosystems (Chapters 3 and 4).

Scientific estimates of future ozone and UV radiation levels rely on scenarios of declining ODSs resulting from continued adherence to the Montreal Protocol and its Amendments. However, a recent study[147] reported unexpected and persistent increases in global emissions of CFC-11, questioning the existing ODS-reduction scenarios. Moreover, the continued growth in the atmospheric concentrations of dichloromethane (CH_2Cl_2), a chlorocarbon not controlled by the Montreal Protocol, could offset some of the future benefits of the Montreal Protocol and lead to a substantial delay (more than a decade) in the recovery of stratospheric ozone over Antarctica.[90] At present, effects on UV-B radiation due to the recently reported emissions in CFC-11 cannot be quantitatively estimated because the effects on ozone have not yet been quantified.

1.3.2 Indirect effects – the Montreal Protocol and climate

Chlorofluorocarbons (CFCs) and some of their replacements are potent GHGs. Therefore, by controlling them, the Montreal Protocol has not only been beneficial for stratospheric ozone and UV radiation at the Earth's surface, but also useful in mitigating global temperature rise and other effects associated with climate change. Measurements in discrete air samples at ground-based stations across North America and by aircraft in the remote atmosphere have shown that ODSs decreased by about 40% from 2008 to 2014.[91] However, the more recent emissions of most hydrofluorocarbons (HFCs; ODS replacements, which do not destroy ozone but have still considerable global warming potentials) have been increasing over the

3 The UV Index (UVI) provides to the public a simple, dimensionless quantity to report the levels of the erythemally-weighted (or "sunburning") irradiance. It is calculated by multiplying the erythemally weighted irradiance expressed in units of W m^{-2} by 40.

same period. The phase-out of HFCs by 2030, in accordance with the provisions of the Kigali agreement,[219] is projected to reduce the climate impacts of HFCs in the upper troposphere and stratosphere by 90% by the year 2050,[95] and to avoid additional warming near the Earth's surface of up to 0.5°C by 2100.[233]

Large effects on climate near the Earth's surface that would have occurred in the absence of the Montreal Protocol have been estimated by several chemistry-climate model (CCM) studies.[76, 148, 154] These studies showed that the Montreal Protocol helped to avoid a further strengthening of the Southern Annular Mode (SAM)[4] as well as further enhancement of the warming in the lee of the Antarctic Peninsula. In the Arctic, the avoided loss of stratospheric ozone due to implementation of the Montreal Protocol is associated with a warming of the Arctic Ocean and North America, and a cooling over Western Europe and Siberia. These projected changes are comparable with those expected by 2025 due to GHGs.[148]

More recent studies have investigated specific impacts on climate near the Earth's surface that have been mitigated by the Montreal Protocol. For instance, a single model study found that, without the Montreal Protocol, the additional radiative forcing (global warming) from CFCs and additional ozone depletion (stratospheric cooling) would have driven large changes in the hydrological cycle, with the sub-tropical dry zones becoming drier and the mid-latitude wet zones becoming wetter.[230] A related study with a similar model[166] projected that the intensity of tropical cyclones would have been three times as large by the year 2065 without the Montreal Protocol, although this effect was dominated by the global warming effect of CFCs, with a minor role for the (considerable) stratospheric cooling. Projections of climate change in the absence of the Montreal Protocol have shown an additional global mean warming of > 2°C by 2070, due to the large increases in radiative forcing from increasing ODSs.[76] These unintended benefits of the Montreal Protocol in mitigating climate change mean that some of the large economic costs from climate damage have been avoided.[155, 199] However, some of the replacement compounds (HFCs) are also potent GHGs that are now controlled by the Kigali Amendment.

1.4 Climate and chemical effects on stratospheric ozone

Increasing concentrations of GHGs, and the resulting climate change, will affect physical and chemical processes important for stratospheric ozone, and therefore UV radiation at the surface. These processes will alter temperatures and abundance of trace gases and, in turn, reaction rates important for ozone levels, as well as the Brewer-Dobson circulation (BDC)[5], which controls the distribution of ozone.[228]

The middle and upper stratosphere cools in response to increasing concentrations of GHGs, in particular carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), due to increased emission of long-wave radiation to space. Outside of the polar regions, this cooling leads to greater concentrations of stratospheric ozone because the rate of catalytic loss of ozone declines with decreasing temperature. For the period 2000–2016, model simulations suggest

4 The SAM is the leading mode of southern hemisphere extratropical climate variability, describing a see-saw of atmospheric mass between the mid- and high-latitudes, with corresponding impacts on the strength of the circumpolar westerly winds. A positive SAM index corresponds to a poleward shift of the maximum wind speed, which results in weaker-than-normal westerly winds in the southern mid-latitudes.

5 The BDC describes a pattern of atmospheric circulation according to which tropospheric air enters the stratosphere in the tropics and then moves upward and poleward before descending in the middle and high latitudes. It explains why tropical air contains less ozone than polar air, even though most atmospheric ozone is produced in the tropical stratosphere.

that increasing concentrations of GHGs account for about half of the observed positive trends in upper stratospheric ozone (35–45 km) of about 2–4% per decade.[228]

At polar latitudes, destruction of stratospheric ozone is drastically accelerated due to heterogeneous reactions on polar stratospheric clouds (PSCs), which form when temperatures in the lower stratosphere drop below a critical threshold. At present, temperatures are generally higher in the Arctic stratosphere compared to the Antarctic, meaning that formation of PSCs is less extensive and less frequent in the Arctic. However, in the future, the region with temperatures below the critical threshold for formation of PSCs may increase significantly, leading to more rapid ozone depletion while levels of chlorine remain elevated.[228]

Stratospheric temperatures in the Arctic are highly variable, with some years already experiencing temperatures low enough for formation of PSCs. Recent examples include the boreal winter/spring of 2010/2011,[129] November and December 2015,[24, 133] as well as January 2016.[128] CCMs suggest that similarly large losses of ozone may sporadically recur until the middle of the 21st century during Arctic winters characterized by a cold and strong polar vortex.[17, 116] Dynamical processes will continue to play an important role in determining levels of Arctic springtime ozone in the future, although halogen chemistry will remain a smaller contributor to stratospheric ozone depletion for many decades.

Model calculations suggest that increasing concentrations of GHGs will increase the strength of the BDC, leading to decreases of ozone in the tropical lower stratosphere and increases at higher (extra-tropical) latitudes.[33] The weight of evidence suggests that the shallow (lower stratosphere) branch of the BDC has strengthened over recent decades, but evidence for strengthening in the middle and upper stratosphere is less clear.[228] Decadal-scale variability in the strength of the BDC will also be important in driving medium-term (next few decades) trends in ozone.[221] Over this century, the magnitude and rate of ozone recovery will depend on the expected reduction in halogenated ODSs as well as on climate changes driven by GHG emissions, and especially through the strengthening of the BDC.[34, 57, 144] One model study has suggested that, by the end of the 21st century, stratospheric ozone over Antarctica may have recovered to levels greater than in 1960, due to an increased dynamical supply of ozone from a strengthened BDC.[144]

Projections of future changes in stratospheric ozone also depend on the direct chemical impacts of the GHGs, methane and N_2O. Increasing concentrations of N_2O destroy stratospheric ozone, while increasing concentrations of methane result in greater formations of ozone in the lower stratosphere and troposphere down to the surface.[228] Future global stratospheric ozone concentrations, and indirectly surface UV radiation (notwithstanding changes in clouds and aerosols in the troposphere), will be largely controlled by the abundance of N_2O and methane in the second half of the 21st century, when concentrations of ODSs are projected to become comparatively small.[34] Overall, the simulated magnitude of these impacts is dependent on the models used,[34, 57, 96] increasing the uncertainty in the projected changes in UV radiation.

Fig. 2 shows recovery of the total ozone column in the future as a function of latitude, as simulated by a selection of CCMs that were included in the fifth Coupled Model Intercomparison Project (CMIP5).[34] Increasing the concentrations of GHGs (RCP[6] 2.6 to RCP 4.5 to RCP 8.5)[98] results in a stronger BDC, which means larger increases in stratospheric ozone

6 Representative Concentration Pathways are greenhouse gas concentration (not emissions) trajectories adopted by the IPCC for its fifth Assessment Report (AR5) in 2014. The pathways are used for climate modelling and research. They describe four climate futures, which differ on how much greenhouse gases are emitted in years to come. The four RCPs, RCP 2.6, RCP 4.5, RCP 6, and RCP 8.5, are named after a possible range of radiative forcing values in the year 2100 relative to pre-industrial values (+2.6, +4.5, +6.0, and +8.5 W m^{-2}, respectively).

at higher latitudes by the end of the 21st century (**Fig. 2(a)**). For the tropics, the change in total ozone column is a combination of temperature-mediated upper stratosphere ozone recovery (strongest in RCP 8.5) versus ozone decreases in the lower stratosphere due to a stronger BDC.[57, 96] In addition, the tropospheric ozone column increases in RCP 8.5, but decreases in RCP 4.5 and 2.6.[96] For RCP 2.6 and 4.5, the ozone column recovers close to mid-20th century values (~1960; **Fig. 2(b)**), with RCP 8.5 exceeding those levels at the higher latitudes.

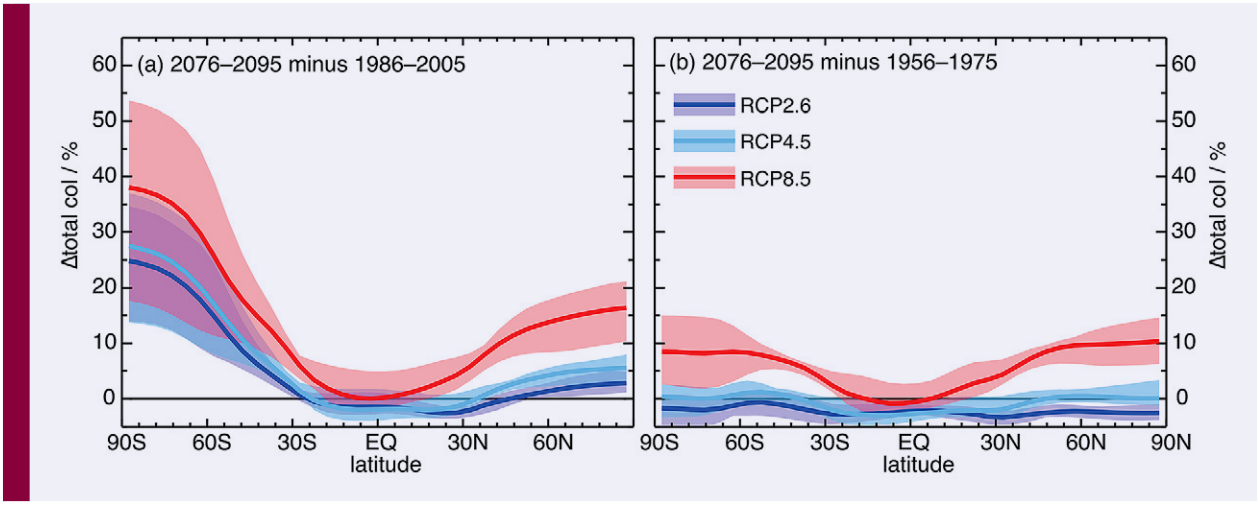

Fig. 2 **Simulated relative change (in %) in total column ozone by the end of the 21st century (2076–2095 average) compared to (a) the strong stratospheric ozone depletion period (1986–2005), and (b) before the strong ozone depletion period (1956–1975). Results are for three RCP scenarios and five different CMIP5 models, showing both the mean change and the inter-model spread. The chosen CMIP5 models all have interactive chemistry and simulate throughout the depth of the stratosphere: CESM1-WACCM, GFDL-AM3, GISS-E2-H (p2), GISS-E2-R (p2) and MIROC-ESM-CHEM. Data are as per Butler *et al.*,[34] their Fig. 1**

Climate changes at the Earth's surface may also be important for stratospheric ozone. Recent work has suggested that loss of Arctic sea ice has contributed to a persistent late-winter shift of the Arctic vortex towards the Eurasian continent over the past three decades,[239] leading to decreases in total ozone over Eurasia and increases over North America, together with the suggestion that recovery of total ozone over Eurasia may be delayed during the first four decades of the 21st century.[241] However, further analysis of these changes in vortex patterns with climate models suggests that, while there may be a small anthropogenic component to the trend in vortex position, this is not linked to the decline of Arctic sea ice.[186] This analysis concludes that the recent trends in the vortex noted by[239] may be primarily a result of unforced internal variability.

Finally, variability in atmospheric circulation patterns also affects the distribution of stratospheric ozone and therefore UV-B radiation. An understanding of the role of interannual variability – and natural variability on longer timescales – is necessary to ascertain when the ozone layer has recovered.[228] One driver of interannual variability is the quasi-biennial oscillation (QBO), which describes an east-west oscillation in tropical stratospheric winds. In the NH winter of 2015/2016 an unprecedented disruption of the QBO was detected,[152, 159, 228] and total ozone measurements by the satellite-borne Solar Backscatter Ultraviolet Radiometer (SBUV) revealed the development of positive anomalies of ozone in the equatorial stratosphere in May-September 2016 and a substantial decrease in ozone

in the subtropics of both hemispheres.[213] As understanding of factors affecting the QBO is incomplete, it is unclear whether recurrence of such a disruption is likely in a changed climate. In general, the magnitude of ozone depletion in Antarctica will continue to exhibit variability at interannual time scales, until ODSs are removed from the stratosphere and the ozone layer has recovered.[228]

Variability in the propagation and dissipation of planetary waves will also alter stratospheric circulation, which affects the distribution and chemistry of ozone over the globe. For instance, the strength of the polar vortex in the SH, and resulting levels of polar ozone depletion, have been shown to be coupled with anomalies in sea surface temperature (SST) in the maritime continent/East Asian marginal seas, which drive anomalous planetary wave behavior.[209] Furthermore, the overall warming of the surface of the ocean in this region could have driven a substantial fraction of observed trend of loss of polar ozone in the SH (~17%) through the anomalously weak propagation and dissipation of planetary waves, and resulting stronger, colder vortex.[209] Variability in planetary waves is also associated with the El Niño-Southern Oscillation (ENSO) and has been shown to be coupled to the zonal distribution of the mid-latitude total ozone column (e.g., increased ozone for the North Pacific, southern USA, northeastern Africa and East Asia, but decreased ozone over Europe and the North Atlantic during El Niño events).[240]

2 Effects of changes in stratospheric ozone on UV radiation and climate

Changes in stratospheric ozone have been a major driver of changes in clear-sky UV-B radiation, especially at high latitudes where ozone exhibits its highest variability. Depletion of stratospheric ozone resulting from emissions of ODSs into the atmosphere has led to latitude-dependent increases in UV-B radiation at the Earth's surface, particularly in the 1980s and 1990s. Such increases in UV-B radiation have been measured at various locations and have been extensively discussed in previous assessment reports.[215–217, 224, 225] Over some regions, direct correlations between ozone and UV-B radiation could not be detected in measurements because they were masked by other factors that are also strong attenuators of UV-B radiation, as discussed in section 3. The changes in ozone that have occurred over the past decades resulted in changes in UV-B radiation at the Earth's surface and in surface climate, with consequences for human health, marine and terrestrial ecosystems, as well as in tropospheric chemistry, biogeochemical cycles, and materials. These impacts are discussed in Chapters 3–7). This section assesses literature on the impacts of recent ozone changes on climate and UV radiation, whereas future projections are discussed later.

2.1 Effects of Antarctic stratospheric ozone depletion on climate

There is now general agreement that the recurrent ozone 'hole' in the Antarctic stratosphere in spring is a major driver of observed changes in atmospheric circulation in the SH summer.[228] These changes are affecting the climate near the surface in various ways, and future projections of their impact depend on the rate of recovery of ozone *versus* the rate of increase of GHGs. Increased concentrations of ODSs and depletion of ozone over Antarctica in the late 20th century have been recognized as important drivers of changes in climate in

the SH and have been suggested as explanations for the observed changes in circulation, temperature, and salinity of the Southern Ocean.[187, 193]

2.1.1 Shifting of climate zones

Well-established changes in climate due to depletion of Antarctic ozone include a strengthening and poleward contraction of the westerly atmospheric circulation over the southern extratropics (all latitudes except the tropics) during austral spring and summer. This corresponds to a trend towards the positive index of SAM, leading to associated effects on temperature and precipitation in the mid-latitudes extending into the subtropics and even the tropics. New studies have reconfirmed these overall effects using different approaches based on observations and models.[189, 196]

Long-term data records show that changes in tropospheric circulation due to the ozone 'hole' have contributed to a decrease in summer temperatures over southeast and south-central Australia, and inland areas of the southern tip of Africa.[14] In the decades since the appearance of the ozone 'hole', anomalously high (or low) total ozone column amounts in the spring are significantly correlated with hotter (or colder) than normal summers over large regions of the SH. These patterns are related to the SAM.

Depletion of stratospheric ozone in Antarctica has been shown to explain more than half of the observed changes in precipitation between 1979 and 2013 in the subtropics of the SH, while increasing concentrations of GHGs have a weaker role.[11] This finding emerged from a statistical modelling approach (maximum covariance analysis) that was used to quantify the relative contribution of different climate forcing mechanisms, including ozone depletion, changes in the sea surface temperature of the equatorial Pacific, and increasing GHGs. In a more recent study,[29] an analysis of observations and climate models demonstrated that depletion of stratospheric ozone has led to changes in springtime precipitation in the sub-tropical South Pacific Ocean, Australia, and New Zealand over the 1961–1996 period. These changes range from –25% to +40% depending on location. Despite the large variability in the magnitude of impact among climate models, they all indicate a consistent pattern of changes over this region. Furthermore, qualitative agreement between models and measurements suggests that these effects on precipitation will likely reverse when ozone recovers in the future.

South-eastern South America experienced the highest increase globally in extreme summer rainfall over the 20th century.[120] An analysis of an ensemble of 12 simulations by one climate model suggests that this increase in extremes of maximum precipitation, as well as a decrease in the extremes of maximum temperature, over the second half of the twentieth century were driven by the changes in tropospheric circulation induced by depletion of stratospheric ozone.[229] This supports previous studies,[78, 103] and, although it is at odds with a similar study[238] in its attribution of the effect to ozone depletion, it draws its evidence from a larger model ensemble and analysis of a period more appropriate to the impact of ozone depletion.

Changes in the tropical atmospheric circulation caused by Antarctic ozone depletion and increasing GHGs have resulted in a poleward shift of the boundaries of sub-tropical and tropical climatic zones. A recent modelling study[206] has confirmed previous work and showed that the observed poleward expansion of the Hadley[7] circulation cell is caused mainly by

7 The Hadley circulation is a large-scale atmospheric convection cell in which air rises at the equator and sinks at medium latitudes, typically at about 30° northern or southern latitudes.

these two anthropogenic forcing mechanisms, rather than by natural forcing. As with the changes in SAM, the ozone depletion in the Antarctic ozone 'hole' was found to dominate the expansion of the southern Hadley cell in the austral spring and summer, with a smaller contribution from Arctic ozone depletion for the northern cell in boreal spring.

Linkages between stratospheric ozone depletion and tropospheric changes have previously been reported for the austral summer months (December-February). A new study has shown that this effect persists through to the autumn.[99] This study reported a poleward shift in the position of the jet stream (i.e., a positive SAM index) during May, driven by the stratospheric cooling associated with Antarctic ozone depletion. However, mechanistic descriptions of the dynamical drivers for the trend, including why the significant trends favour particular months, remain to be provided.

The continued expansion of the Hadley cell expected from increases in GHGs will be slowed by recovery of stratospheric ozone. This modification of the Hadley cell will modify the boundaries of the climatic zones, leading to expansion of subtropical dry zones to higher latitudes, affecting terrestrial and aquatic ecosystems (see Chapter 3).

2.1.2 Effects on Antarctic sea-ice-cover

Changes in sea ice are important for UV-B radiation. Increases in the extent of sea ice lead to increased UV-B radiation above the surface, but to decreased radiation penetrating the water under the ice, with implications for terrestrial and aquatic ecosystems. There is no consensus with respect to the contribution of the ozone 'hole' to the observed increase in the extent of sea ice around Antarctica between 1979 and 2014, which was followed by a dramatic decline between 2014 and 2017.[212] Preliminary data suggest that the extent of sea ice in 2018 was similarly low to that observed in 2016 and 2017 (https://neptune.gsfc.nasa.gov/csb/index.php?section=234). Climate model simulations with realistic ozone depletion do predict decreases in sea ice,[193] but do not capture the regional patterns in trends.[115] Consequently, confidence in the ability of models to accurately simulate the response of sea ice to ozone depletion is low.[228]

There has been progress in our understanding of the physical processes that link ozone depletion to sea-ice-cover trends. Based on analysis of idealized climate model simulations, two processes operating on different time scales have been proposed.[67, 228] In the short-term (a few years to a few decades, depending on the model), changes in ocean circulation induced by depletion of stratospheric ozone cool the sea surface around Antarctica, leading to expansion of the sea ice, as well as to upwelling of warm waters in the region of the seasonal sea ice. This pattern is consistent with the well-known relationship between SAM and sea ice or ocean surface temperature. In the long-term (multiple decades), the effect resulting from upwelling of warm water begins to dominate, slowly leading to warming of the ocean and ultimately to long-term reduction of sea ice. The short/long-term behavior has been noted in other climate model studies,[187, 188] although the characteristic time scales of each process vary greatly between different models.[88] The impact of SAM on sea ice remains unclear.

A more detailed discussion on the relevant physical mechanisms and model results for relationships between ozone and sea ice is presented in the WMO Scientific Assessment Panel Report.[228]

2.1.3 Direct effects on solar radiation at the Earth's surface

A modeling study[43] investigated the direct effect of the Antarctic ozone 'hole' on total solar radiation. Weaker absorption by the smaller amounts of ozone in the stratosphere leads to increased UV radiation at the Earth's surface. The contribution of the increased UV radiation to total solar radiation at the surface has been estimated to 3.8 W m^{-2} (about 2%) in October–December. However, for the highly reflecting surface of Antarctica,[79] most of this excess radiation is redirected upwards and does not contribute significantly to increases in air-temperature near the surface.

2.2 Effects of recovery of Antarctic ozone on UV radiation

The beginnings of Antarctic ozone recovery have been reported and discussed in several studies,[228] and it is expected that UV-B radiation at the surface will decrease as ozone increases. However, so far there has been no evidence of reductions in UV-B radiation over Antarctica in response to ozone recovery. As noted in section 1.4, the magnitude of Antarctic ozone depletion, and corresponding effect on UV-B radiation, will continue to exhibit variability at interannual time scales until the ozone layer has recovered.[228] The enhanced ozone depletion seen in 2015 due to aerosols from the eruption of Calbuco in southern Chile[101, 195, 201] demonstrates the continued importance of episodic impacts on the Antarctic stratosphere while ODSs are still present.

2.3 Effects of Arctic ozone losses on UV radiation and climate

The recently observed transient depletion of stratospheric ozone in the Arctic led to increased UV-B radiation at the Earth's surface and may have contributed to changes in the surface climate of the NH. As discussed in the previous assessment report,[12] unprecedented decreases in stratospheric ozone for the region were observed over the Arctic in winter 2010/11 due to unique meteorological conditions,[129] and have influenced UV radiation in the summer of 2011.[104] Smaller decreases in ozone occurred again in the winter of 2015/16,[128] albeit with different timing. During the second half of February 2016, the total ozone column was reduced by more than 30% relative to the historical (2005–2015) mean over Northern Scandinavia and Northern Siberia. This led to an increased UVI at the surface of up to 60% over an area roughly matching the region where ozone was abnormally low. However, absolute increases remained below 1 UVI unit because the event occurred early in the year when solar elevation angles were low.[24]

Analysis of measurements of ozone in 1979–2012 revealed a statistically significant association (at the 95% level) between low concentrations of Arctic stratospheric ozone in March and changes in climate between 30 and 70°N in March and April.[100] The changes include a poleward shift of the North Atlantic jet stream, lower-than-normal surface temperatures over eastern North America, southeastern Europe, and southern Asia, and higher-than-normal temperatures over northern and central Asia. Another study[232] suggests that effects from variations in Arctic stratospheric ozone may extend even to the tropics and may be associated with El Niño Southern Oscillation (ENSO) events. However, neither study has demonstrated causality between the identified associations. Moreover, further investigation

is needed to disentangle the role of sea-ice loss[15, 72] and interannual variability[186] for northern mid-latitude changes associated with the jet stream and vortex.

3 Factors other than ozone that affect UV radiation

Apart from ozone, the important determinants for UV radiation at the Earth's surface are clouds, aerosols, and surface reflectivity. These factors are strongly related to anthropogenic activities that have led to increased emissions of GHGs and changes in particles released into the atmosphere, which are expected to change in the future. UV radiation is also determined by the 11-year solar cycle and long-term changes in solar activity, both directly and indirectly through influences in stratospheric ozone. The variability and importance of these factors for UV radiation reaching the Earth's surface have been discussed already in previous reports.[12, 138] Here we present a summary of recent studies on key properties and mechanisms as they relate to effects on UV radiation, and are essential for estimating ambient levels of UV radiation.

3.1 Clouds

Clouds are by far the most important attenuators of solar radiation reaching the troposphere across all wavelengths. Thick clouds can diminish radiation to levels close to zero, while thin clouds can lead to reductions of at least a few percent. New studies have improved understanding of the effects of clouds on UV radiation and the physical mechanisms of the processes involved. The weak wavelength dependence of the optical depth of clouds predicted by theory has been confirmed with measurements.[183] In this study, the optical depth of clouds at a given instance was determined by iterative comparisons of the measured irradiance to estimates of irradiance from a model based on a range of optical depths of clouds. Measurements under overcast conditions at Valencia, Spain, indicate that the attenuation by clouds is 2% smaller for erythemal irradiance than for total solar irradiance. Even though optical depth of clouds is almost independent of wavelength, the effect of clouds on solar irradiance reaching the surface is wavelength-dependent because of interactions of the cloud with the Rayleigh-scattering of radiation by the air-molecules.[114, 122] Due to wavelength-dependent effects, clouds can modify the sensitivity of erythemal radiation to variations in total ozone. For example, a recent study for Granada, Spain, reported that erythemal irradiance showed a greater sensitivity to ozone with increased cloudiness.[4]

There has been confusion in the recent literature about the magnitude and wavelength-dependence of the effects of clouds on UV radiation. To clarify this issue, high-quality spectral measurements obtained from instruments at several sites covering a wide range of altitudes (up to 3.4 km at Mauna Loa Observatory in Hawaii) were used to analyze the wavelength dependence of cloud effects on UV radiation.[137] During partly cloudy conditions when the sun is not obscured, radiation at the Earth's surface for all wavelengths can be significantly higher than for clear-sky conditions because bright clouds scatter more radiation towards the surface than the blue sky. Such events can last for a few minutes or even longer, depending on the type of cloud and speed of its movement. These enhancements of radiation by clouds tend to be smaller in the UV-B than in the UV-A (315–400 nm) or visible regions, mainly because the proportion of the direct radiation (which is responsible for the enhancement) in the UV-B is smaller than for the longer wavelengths. In snow-free conditions, enhancements

greater than 20% are rare in the UV-B region, but can reach 40% in the UV-A region.[10, 137] Enhancements by clouds can be even larger in the visible region, but they rarely exceed 50%.[10, 37, 137] These results are consistent with earlier studies.[51, 164] "Cloud enhancement" events can substantially increase exposure to UV radiation for short periods, so can be important for exposure of humans and ecosystems. However, over longer periods (e.g., over the course of a day), the presence of clouds usually reduces the total dose of UV radiation.

Clouds scatter back (upwards) a large portion of the incoming solar radiation. The effective albedo caused by clouds below a mountain summit has been quantified using measured and modeled UV irradiance data from the Izaña observatory (28°N, 2400 m above sea level).[75] The largest observed effective albedo value in the UV was found to be 0.58 (i.e., 58% of incident radiation is reflected upwards). More typical values range between 0.2 and 0.5 and are about 10 times larger than the local surface albedo (0.02–0.05).

Measurements combined with radiative transfer modeling confirmed theoretical predictions from Mie theory that clouds composed of small water droplets attenuate UV radiation more efficiently than clouds composed of large droplets, for the same liquid water content.[132] The magnitude of this effect depends on solar zenith angle and liquid water content, which determine the optical thickness of the cloud in the path of the radiation. Clouds in highly polluted atmospheres tend to consist of more, smaller cloud droplets (compared to clean atmospheres) and can last longer because they are less likely to produce rain.[3]

Better understanding of the wavelength-dependent effects of clouds on radiation received at the ground will allow more accurate quantification of how different biological or chemical weightings of radiation respond to changes in cloudiness. This may be important in the coming decades, as global cloud patterns and characteristics are projected to change due to climate change.[98]

3.2 Aerosols

3.2.1 Effects of aerosols on UV radiation

Aerosols (solid and liquid particles suspended in the atmosphere see Chapter 6) play a significant role in attenuating UV radiation and in modifying the fraction of its diffuse component. The optical properties of aerosols depend on their size, shape, and chemical composition. Quantifying the effect of aerosols on UV radiation at the Earth's surface requires knowledge of the total aerosol optical depth (AOD or τ; dimensionless) and its absorption efficiency (SSA).[8] The dependence of UV irradiance on AOD, SSA, wavelength and measurement geometry (horizontal, spherical, vertical cylinder) was discussed in detail in the last Assessment.[169]

Measurements of SSA at wavelengths in the UV-B are difficult because aerosol absorption must be separated from the absorption by gases, including ozone, as well as nitrogen dioxide (NO_2) and sulfur dioxide (SO_2), which are typically also abundant in polluted regions. The dearth of observations of SSA and its wavelength dependence is therefore one of the largest

8 The AOD is the sum of the absorption optical depth τ_{abs} (which quantifies the attenuation of the direct solar beam due to absorption of photons) and the aerosol scattering optical depth τ_{sca}: ($\tau = \tau_{sca} + \tau_{abs}$) The wavelength dependence of τ is often parameterized by a simple power model: $\tau \propto \lambda^{-\alpha}$, where the Ångström exponent α quantifies the wavelength dependence of τ. The value of α is often determined from measurements in the visible, and extrapolation to UV wavelengths is subject to uncertainties. Instead of specifying τ and τ_{abs}, the single scattering albedo (SSA) is often reported: $SSA = \frac{\tau_{sca}}{\tau_{sca}+\tau_{abs}} = \frac{\tau_{sca}}{\tau}$, resulting in: $\tau_{abs} = (1 - SSA) \times \tau$. A decrease in SSA, therefore, corresponds to an increase in absorption of radiation.

uncertainties in estimating surface UV irradiance or projecting future levels of UV radiation in regions with high levels of air pollution.

Fig. 3 shows measurements of the SSA at Santa Cruz, Bolivia.[146] The decrease of SSA towards wavelengths in the UV-B is qualitatively similar to that reported in our last assessment[217] and recent measurements at Athens, Greece.[106] However, measurements of SSA in the UV-B like those reported in these two studies[106, 146] are rare, and absolute values of SSA can vary significantly depending on the chemical composition of aerosols. For example, organic aerosols (i.e., aerosols that contain organic carbon material) exhibit a large wavelength dependence in the UV-B compared to other aerosol types.

The The highly non-linear changes in SSA with wavelength have important implications for calculating the effect of aerosols on UV radiation. Their effect will be seriously underestimated if SSAs measured at longer wavelengths are simply extrapolated into the UV-B region. As discussed in the previous report,[12] at least 20% of the observed difference in UV-B radiation between New Zealand and rural USA was attributable to aerosol effects, despite the relatively small difference in AOD between the sites.

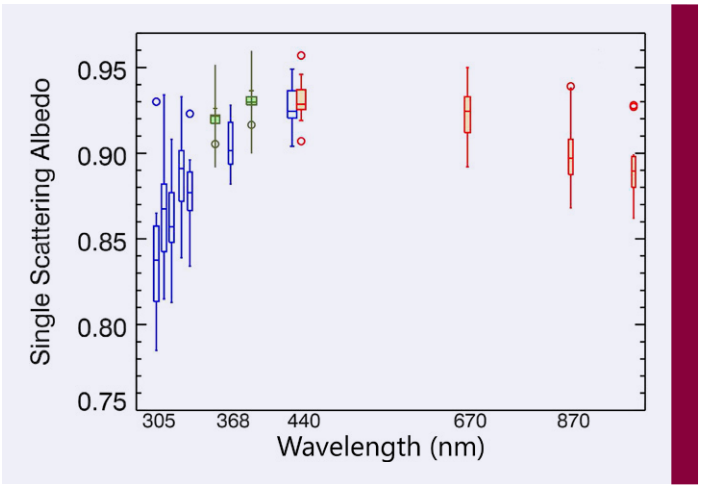

Fig. 3 **Spectral dependence of smoke aerosol single scattering albedo (SSA) derived from ground-based and satellite observations during the field campaign in Santa Cruz, Bolivia, in September–October 2007. Data are from a UV-MFRSR instrument (blue), AERONET (red), and OMI (green). All data are shown as box-whisker plots. Boxes are the interquartile range (IQR; 25 to 75 percentiles) and whiskers are stretched to the maximum and minimum within 1.5 times the IQR. The circles show the outliers. (Adapted from ref. [146]) Measurements of SSA from the ground (UV-MFRSR, AERONET) are more reliable than measurements from space (OMI) because of the difficulty to probe the lower troposphere with satellites.**

Most pronounced effects of aerosol occur near the sources of emission, but significant influences have been identified on regional and global scales due to transport of aerosol. Changes in the amount and optical properties of anthropogenic aerosols have been observed at multiple locations worldwide. Data from the AERONET network revealed decreases in the amount and absorption efficiency of aerosols (quantified by the SSA) at most stations since 2000.[9, 118, 131, 168] These changes were caused by decreases in air pollution which would be expected to have led to increases in UV radiation at the surface. However, at most locations, no UV radiation data are available to assess these effects quantitatively.

Measurements at seven stations in the USA over 1995–2010 indicated a positive trend in diffuse irradiance, despite there being no trend in clear-sky direct solar irradiance.[74] It was hypothesized that this finding was a result of growth in air traffic over the USA which increased the amount of cirrus clouds.

As changes in total ozone over mid-latitudes have been generally small since the onset of ozone depletion, changes in the attenuation of UV-B radiation under cloud-free skies in most populated areas are mainly controlled by the concentrations of aerosols and the wavelength

dependence of their optical properties. Data from a multi-filter shadow-band radiometer and a sun-photometer have been combined to quantify the absorption efficiency of aerosols over Athens, Greece, at selected wavelengths in the UV-A, visible and near-infrared ranges (332–1020 nm). The largest absorbing efficiency was found for organic and dust aerosols,[106] confirming results of a previous study,[172] which showed that desert dust can attenuate the direct UV irradiance at 400 nm by up to 55% and increase the diffuse irradiance by up to 40%.

At many locations over China, the amounts of aerosol remain high. The AOD at 440 nm has ranged between 0.3 and 1.0 and has exceeded 5.0 during extreme events in some locations, but with no significant trend since 2002.[169] Analysis of recent ground-based and satellite observations over East China for 2005–2015[119] suggests that the AOD was decreasing over this period, leading to increases in total solar radiation. Data from XiangHe in North China suggest that decreases in the optical depth and increases in the single scattering albedo (smaller absorbing efficiency) of aerosols have contributed to the observed increases in the direct and diffuse solar radiation. It is difficult to extrapolate these findings to the UV region, since scattering by aerosols affects UV radiation differently than visible.[217]

A climate-change-driven increase in the frequency and extent of wildfires[1, 68, 84, 94] could be an important source of aerosols, with significant effects on surface UV radiation. Carbonaceous aerosols resulting from combustion include black carbon (BC), which is primarily released at elevated temperatures, and brown carbon (BrC), which is produced by the burning of organic matter at lower temperatures such as in forest fires (see Chapters 4 and 5). Both aerosol types can strongly absorb UV-B radiation. By considering the different fractions of BC and BrC over Santa Cruz, Bolivia, it was found that absorption by BrC caused a further 20–25% reduction in irradiance at 305 nm compared to the BC-only absorption.[146] If confirmed, unaccounted reduction in surface UV-B irradiance by BrC could be important when assessing health risks due to exposure to UV-B radiation. The wavelength dependence of the absorption of UV and visible radiation by BC was previously believed to be relatively small, decreasing proportionally to the reciprocal of wavelength ($1/\lambda$).[18] However, measurements from the ground and space for Santa Cruz, Bolivia, indicate that the absorption by BrC has a strong wavelength dependence in the UV with the largest absorption observed at the shorter UV-B wavelengths.[146] Greater effects of aerosols on UV than on visible radiation were also shown by measurements influenced by the smoke plume of the California Rim Fire (encompassing Stanislaus National Forest and Yosemite National Park) on 27 August 2013.[223] Measurements at Lake Tahoe (located 120 km away from the wildfire) showed that, over a period of about 10 days, UV-B radiation was more strongly reduced than visible radiation, albeit with high variability due to changes in wind direction and thickness of the smoke plume. At times, the UV-to-visible ratio was reduced by almost 50%. Such events, which may become more frequent in a warmer and drier climate,[1, 68, 84, 94] are important because by attenuating the UV and visible radiation received at the ground and by regulating the ratio of UV-to-visible radiation in the environment they can affect important biological processes, for instance, the emissions of biological volatile organic compounds (see examples in Chapters 2–5).

Modeling studies have projected that, due to climate change, summertime concentrations of BrC aerosol over the western United States will increase by 40–70% and concentrations of BC aerosol by 20–27% by 2050, relative to the present.[197, 234] Most of this increase (75% for BrC and 95% for BC) is caused by larger emissions from wildfires. Such increases in carbonaceous aerosols would lead to significant reductions in surface UV radiation. For instance, a recent study has shown that wildfires in Russia in 2010 caused reductions of up to 50% in the daytime averaged photolysis rates of NO_2 and ozone along the aerosol plume, driven by

reduced UV radiation.[162] Both types of carbonaceous aerosols can be transported across the globe and persist in the atmosphere for days to weeks (see Chapters 5 and 6). Inclusion of emissions from fires in climate models increased the predicted global mean annual aerosol optical depth at visible wavelengths by 10%.[211]

Besides their role as condensation nuclei in the formation of clouds, aerosols may also interact with cloud droplets resulting in changes in the albedo of clouds, which in turn affects the fraction of solar radiation scattered upwards. Model results have shown large increases in the albedo of clouds with increasing concentration of aerosols that are related to changes in the water content of clouds and in the size distribution of cloud droplets.[73] With respect to the origin of aerosols, anthropogenic sulfate aerosols had a greater effect on albedo of clouds than non-sulfate aerosols.

Future changes in concentrations of atmospheric aerosols used in climate modeling studies depend on the assumed RCP scenario. For the RCPs 8.5, 4.5 and 2.6, the aerosol content is projected to decline strongly and monotonically during the 21st century, after peaking around 2010, while for RCP 6.0 the peak occurs later, around 2050.[204] Consequently, the importance of aerosols in modifying solar UV radiation will become weaker during the 21st century for RCPs 8.5, 4.5 and 2.6. For RCP 6.0, the greater projected AOD for the future would result in reduced UV radiation compared to other RCPs. The aerosol optical properties, such as SSA, asymmetry factor and Ångström exponent might also change in the future, but this information is not included in the RCPs. Lack of information on how these optical properties of aerosols will change over time increases the uncertainties of simulations of UV radiation for the future, which are further affected by the poor knowledge of the wavelength-dependence of SSA.

3.2.2 Advances in the monitoring of aerosols

The tools available for quantifying concentrations of aerosols and the wavelength dependence of their optical properties are still inadequate. The need for development of methods and instrumentation to quantify the absorption efficiency of aerosols at UV wavelengths has already been discussed in previous assessments.[216, 217] Algorithms to calculate the AOD from measurements of instruments of the European Brewer Network have recently been improved and harmonized.[125] Results from two intercomparison campaigns suggest that a well-maintained and calibrated Brewer instrument is capable of measuring AOD with a precision of 0.005 and an uncertainty of 0.04 in the UV range from 310 to 320 nm, with the corresponding values for 306 nm being slightly worse, 0.01 and 0.05, respectively.

A new sun-photometer (ultraviolet precision filter radiometer, UVPFR) developed at PMOD/WRC Davos, Switzerland has been extensively evaluated during two campaigns in Izaña-Tenerife, Spain, in 2015 and 2016, and compared with a Brewer spectrophotometer. It was found that both instruments can measure the aerosol optical depth (AOD) with 0.01 precision at UV-B wavelengths between 305 and 320 nm.[38] Further, a new method has been proposed to enable more accurate calibration of AOD sun-photometers at locations with high and variable aerosol load.[242] Finally, in an intercomparison campaign held in Davos, Switzerland, in autumn 2015, most of the instruments measuring the AOD at visible wavelengths (500 and 865 nm) agreed to within 0.005 units of AOD, while two thirds of the instruments reporting AOD in the UV-A (368 and 412 nm) achieved that goal.[105] Such improvements in instrumentation and methods will facilitate clearer separation of the effects of ozone and aerosols on UV-B radiation.

3.3 Surface reflectivity

Variations in the reflectivity of the Earth's surface (over land and ocean) can lead to variations in incident downwelling irradiance because a fraction of photons that are reflected upward by the reflecting surface is scattered downward by air molecules, aerosols, and cloud droplets. This effect is more pronounced when the surface is covered by fresh snow or ice.

At Barrow, Alaska (71°N), changes in snow cover observed during the last 25 years have had a profound effect on surface UV radiation as illustrated in **Fig. 4**. At this site, there are indications that the onset of persistent snow cover at the beginning of winter has advanced by 8 ± 7 (± 2σ) days per decade (blue dataset in **Fig. 4**, plotted on an inverted scale). In response, the monthly mean UV-A irradiance for October (red dataset in **Fig. 4**) has decreased by 8 ± 4% per decade. This decrease cannot be attributed to changes in ozone and is largely the result of a longer snow-free period in October.[19] For the period 1995–2014, there is a significant anti-correlation (R^2 = 0.56) between the onset of persistent snow cover and monthly mean UV-A irradiance.

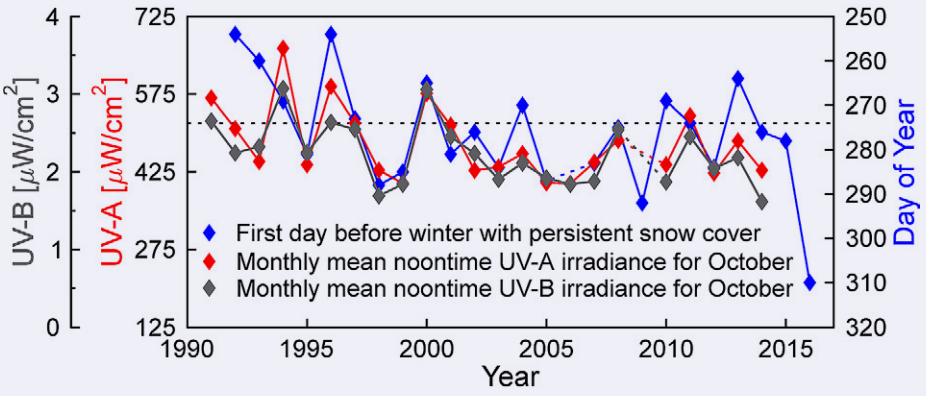

Fig. 4 **Comparison of UV-B (grey symbols) and UV-A (red symbols) irradiance at Barrow with the timing of snow cover onset (blue symbols, right axis), defined as the first day before winter when the surface albedo becomes larger than 0.6 and stays above 0.6 for the rest of the winter. Note that the right axis is inverted. The dotted horizontal line indicates 1 October. The figure is adapted from Bernhard[19] and updated with data from 2010–2016. Surface albedo was measured with pyranometers that are part of the Baseline Surface Radiation Network (BSRN). UV measurements are not available for 2009, 2015, and 2016.**

Based on data from different satellites, statistically significant (at the 95% level) negative trends in UV reflectivity were found for areas in the Bellingshausen/Amundsen Seas near Antarctica, with sea-ice coverage greater than 30%.[53] Although these estimates include radiation reflected by clouds, the air molecules and the surface, reflection by bare or snow-covered sea ice was the main driver of the observed variability in reflectivity. This study reported a reduction in UV reflectivity of up to 3.6 ± 1.0% per decade due to reduction in the concentration of sea ice for the period 1980–2012 in March. On the other hand, positive trends were found for ice-free areas and for areas with low ice-coverage for the entire Southern Ocean. Since the trend in reflectivity in ice-free regions within the 50°–60°S latitudinal band is also generally positive, it is possible that a small increase in cloud amount and/or opacity occurred in the Southern Ocean during the examined period. Finally, the trends over areas with high concentrations of sea ice over this latitude band are mostly negative, although often not statistically significant at the 95% level.

The observed biases in the representation of variations in the surface albedo in the CMIP5 climate models when compared to measurements raise doubts about the reliability of future projections by these models with respect to responses due to the development of sea ice. This conclusion arose from a study focused on the evaluation of spatial and temporal variations in the albedo of ice in the CMIP5 models during the Arctic summer against satellite observations (CLARA-SAL) of surface albedo for the period 1982–2005.[108] Although many individual models show large biases, the mean values of CMIP5 ensemble agree relatively well with the satellite data. However, the good agreement may be serendipitous considering that the discrepancy between individual models and the observations is not well understood.

Over areas currently covered by ice or snow, particularly over high latitudes and high altitudes, reduction of reflectivity of the Earth's surface in the future will lead to decreases in downwelling UV radiation. Local ecosystems should receive less UV radiation in the future, but current models are unable to provide accurate projections of changes in reflectivity.

3.4 Solar activity

The pervious EEAP report concluded that the direct influence of solar activity on the UV-B radiation at the surface is small, but indirect effects, through changes in the formation of ozone initiated by the absorption of solar UV-C (100–280 nm) radiation in the upper stratosphere could be more important. Furthermore, it was suggested that a grand solar minimum that might occur in the future could influence the global climate and the ozone layer, leading to increases in UV-B radiation at the surface. A new modeling study for the period 2000–2199, investigated the influence on ozone and climate by a hypothetical strong decline in solar activity that would last until 2199.[7] It was found that a reduction of about 15% in solar UV-C radiation would lead to a decrease in formation of ozone by up to 8%, which would overcompensate the anticipated increase in stratospheric ozone due to reduced stratospheric temperature and acceleration of the BDC. This would lead to a delay in the recovery of total ozone from ODSs, with global ozone not returning to pre-ozone-'hole' values before the end of the grand solar minimum. Although UV-B radiation at the top of the atmosphere is expected to decrease slightly during a grand solar minimum due to weaker emission from the sun, the effect on UV-B radiation from decreasing total ozone is stronger, resulting in an overall increase of UV-B radiation at the surface. Moreover, during a grand solar minimum, the flux of energetic electrons would diminish, leading to less destruction of ozone by NO_x in polar regions.[8] The effects of changes in high energy electrons due to reduced solar activity have not been fully evaluated yet.[7]

3.5 Effects of climate change on surface UV radiation

Climate change affects surface UV radiation by altering the amount and distribution of ozone, cloud cover and type, aerosol abundance, and surface reflectivity. This section assesses the impact of climate change on drivers other than ozone, which was discussed earlier.

In agreement with simulations from climate models, several independent satellite records indicate that changes in large-scale patterns of clouds have already occurred between the 1980s and 2000s.[156] Between latitudes of 60°S and 60°N, observed and simulated changes in cloud patterns are consistent with poleward retreat of mid-latitude storm tracks, widespread reduction in cloudiness at mid-latitudes between about 30° and 50° of both hemispheres

(presumably leading to increases in UV radiation at the surface), and expansion of subtropical dry zones, as discussed in section 2.1.1 and in Chapter 3. The primary drivers of these changes in clouds are increasing concentrations of GHGs. Over the Arctic ocean, cloud cover increased rapidly during the last 20 years due to warming of the lower troposphere and large reduction of sea-ice cover, which led to enhanced upward transport of moisture.[102] During the period of winter darkness in the Arctic, increased cloud-cover warms the troposphere, and may accelerate the retreat of sea ice, enhancing the feedback processes of Arctic warming.[2]

Apart from their effects on clouds, reductions in ice- and snow-cover, as well as changes in their characteristics (e.g., thickness of ice, depth of snow), influence the exposure of ecosystems to solar UV radiation. Less snow- and ice-cover reduces UV radiation at the surface (due to the lower surface reflectivity) but leads to greater exposure to UV radiation for organisms usually protected under snow and ice. Between 1979 and 2016, the extent of sea ice in the Arctic has decreased at rates of 2.7% and 13.3% per decade in March and September, respectively.[163] Due mostly to later autumn freeze-up, the Arctic sea-ice-free season has lengthened between 1979 and 2013 at a rate of 5 days per decade on average, but with a maximum rate of 11 days per decade in some regions.[203] Over Arctic land areas, the snow cover in June was less than 4 million km^2 only once in the period 1967–2008, but has been below this value every year since 2008.[56]

In the SH, while Antarctic sea ice has been increasing since the start of satellite monitoring in 1978 until 2014, sea-ice-cover decreased dramatically in the last three years, shrinking to an historic low on 1 March 2017.[212] Climate change will also change the extent of ice-free areas on the Antarctic continent, yet the distribution and severity of these effects remain unclear.[117] This study[117] suggests that melting across the Antarctic continent will lead to the emergence of between about 2,100 (RCP 4.5 scenario, lower bound) and 17,000 km^2 (RCP 8.5 scenario, upper bound) of new ice-free area by the end of this century; the upper bound representing nearly a 25% increase. Most of this reduction is projected to occur on the Antarctic Peninsula where the total ice-free area could increase by a factor of three.

Lastly, climate change will affect the abundance of aerosols in the air. For example, the observed increasing frequency and extent of wildfires due to climate change,[1] are important sources of aerosols with significant effects on UV radiation at the Earth's surface. Despite strong correlation between increased drought frequency and occurrence of wildfires,[223] projections of changes in wildfires and associated emissions of compounds and aerosols into the atmosphere are limited in accuracy by the complexity of the processes.[84]

The direct and indirect effects of climate change discussed above do not change UV radiation in simple ways but depend on latitude, season, location, and emission scenario. Projections that take these factors into account are discussed in section 5. Impacts of changes in UV radiation due to these factors are discussed in Chapters 2–7.

4 Variability in UV radiation and trends from observations

4.1 Variations of UV radiation in space and time

UV radiation at the Earth's surface is mostly controlled by the solar zenith angle (SZA), which varies with the time of day, latitude, and season. Seasonal variations in Sun-Earth separation are also significant. Absorption and scattering processes in the atmosphere result in additional variation, as discussed in section 3.

In the previous assessment,[217] latitudinal variations in annual doses of UV-B and UV-A radiation were discussed. These were derived from high-resolution measurements with ground-based spectroradiometers that comply with the quality standards of the Network for the Detection of Atmospheric Composition Change (NDACC).[139] This study has recently been expanded to also include latitudinal variations in the annual erythemal dose.[55] Because UV-B radiation contributes approximately 90% to the erythemal weighting, latitudinal differences in UV-B and erythemal dose show similar patterns, but gradients are larger than for the UV-A dose.

The annual erythemal dose is approximately a factor of four larger in the tropics than at high latitudes.[55] In the tropics, the annual dose reaches about 1.75 MJ m^{-2} near sea-level, which corresponds to an average daily dose of 4.8 kJ m^{-2}. At high altitude sites, much higher doses were measured at the Atacama Desert, Chile (5.2 km altitude),[49] which correspond to about 2.4 MJ m^{-2} of erythemal irradiance. For fair-skinned individuals (skin type I), the minimal erythemal dose (MED) leading to reddening of the skin is about 0.2 kJ m^{-2}.[142] The average daily dose at the equator is therefore about 24 MED for a person with type I skin. The maximum daily erythemal dose ever observed at the Mauna Loa observatory, Hawaii, located at 3,400 m altitude, is 9.5 kJ m^{-2} (or 47.5 MED for a person with type 1 skin).[136]

Despite low solar elevations at high latitudes, annual erythemal UV doses in Antarctica are still significant and can reach nearly half the values at mid-latitudes because of high surface albedo, 24 hours of sunlight in the summer (which occurs when the Earth-Sun separation is at its minimum), the effect of the ozone 'hole', and high surface elevation.[21] For example at the South Pole, the average daily erythemal dose is 1.3 kJ m^{-2} or almost one third of the dose measured in the tropics.[55] However, during the ozone 'hole' periods the maximum dose at the South Pole can reach 7.8 kJ m^{-2} which is similar to that at mid- to low-latitudes.[21]

Vitamin D_3-weighted UV doses (i.e., UV doses relevant for the synthesis of vitamin D in human skin) during winter months in Northern Germany (52°N) and New Zealand's South Island (45°S) have recently been compared.[181] A strong latitudinal effect is expected due to the lower sun elevations at higher latitudes. When corrected for the difference in latitude, the vitamin D_3-weighted exposure in New Zealand during winter is a factor of 2 higher than in Germany, mainly because of greater cloudiness in Northern Germany. However, the attenuation by clouds at European stations at latitudes less than 48°N is smaller than Northern Germany, implying that the difference in UV levels between Europe and New Zealand is less pronounced for these more southern European locations.

Year-to-year variability in UV irradiance at a given location is controlled mainly by variations in ozone concentrations, cloud cover, and aerosols. Variations in ozone and their effect on UV irradiance at the surface are most pronounced at high latitudes. Despite recent evidence that stratospheric ozone concentrations are recovering, the ozone-induced variability of UV-B

radiation in Antarctica remains very large, with near record high UVI observed at the South Pole in spring 2015 and below average UVI in spring 2016 and 2017 (**Fig. 5**). The relatively high UVI values observed in the spring of 2015 were partly caused by a large and long-lasting ozone 'hole'. Chemical depletion of ozone was enhanced in that year by heterogeneous processes associated with the volcanic aerosols that were injected into the stratosphere by the eruption of the Calbuco volcano in Chile,[101, 195] as well as by an unusually cold and undisturbed polar stratospheric vortex.[150]

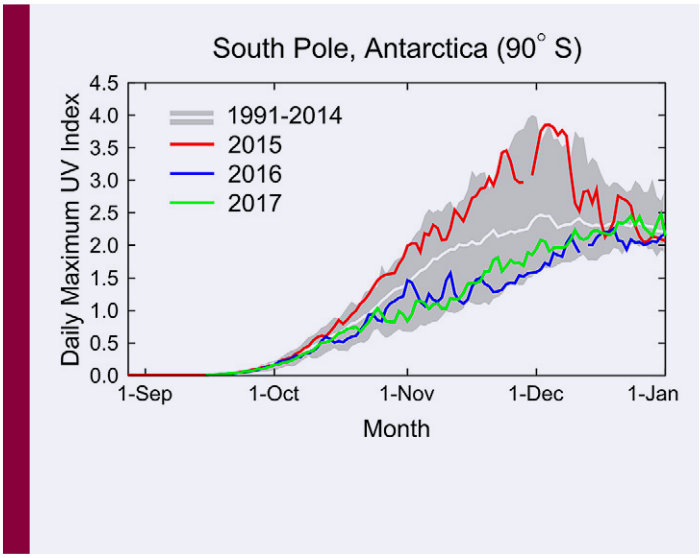

Fig. 5 **Daily maximum UVI measured at the South Pole in 2015 (red line) and 2016 (blue line) and 2017 (green line) compared with the average (white line) and the lowest and highest values (grey shading) of observations of the years 1991 to 2014. Note that the ozone 'hole' first occurred in the 1970s and the reference range of 1991–2014 therefore only includes years when the 'hole' was established. The UVI was calculated from spectra measured by a SUV-100 spectroradiometer located at the South Pole. Up to 2009, the instrument was part of the NSF UV monitoring network[22] and is now a node in the NOAA Antarctic UV Monitoring Network (https://www.esrl.noaa.gov/gmd/grad/antuv/). Consistent data processing methods were applied for all years.**

4.2 Observed long-term changes in UV radiation

Long-term changes in UV radiation have historically been calculated from measurements performed from space and at the ground. Satellite sensors suitable for estimating the UV irradiance at the Earth's surface only became available in the late 1970s. The number of reliable ground-based stations was also small before the ozone 'hole' was discovered. Trend calculations based on direct observations are therefore limited to only the last 38 years or so, with few exceptions.

Changes in UV radiation since 1979 have been derived from a series of polar orbiting satellite instruments for the latitude range of 55°S to 55°N and results were summarized in the last assessments.[12, 138] The UV data are derived mainly by radiative transfer calculations using total ozone, SZA, and information related to surface reflectivity and aerosols. For the period 1979–2010, increases in UVI, evaluated as a function of month and latitude belt (zonal average for every 5° of latitude from 50°S to 50°N), ranged between 0 and +5% per decade. Changes were dominated by increases in the UVI that occurred in the first half of this period when ozone depletion was progressing. Most of the increases are significant at the 95% level except those calculated for winter months of both hemispheres and the equatorial zone where changes are close to zero. The largest positive trends were observed during the spring and summer at mid-latitudes of the SH, where the greatest decrease of ozone within the latitude range 50°S–50°N was observed. Unfortunately, these trend estimates cannot be confirmed with ground-based measurements because observations of UV radiation in the SH started only in 1990, while the largest depletion of stratospheric ozone at southern mid-latitudes had occurred already in the 1980s. Since the late 1990s, when ground-based measurements at

several sites became available, changes in the total column ozone have been small. Reflectivity data from several satellites between 1979 and 2012 suggest that decreases in sea ice and small increases in the amount of clouds over the region of the Southern Ocean around the Antarctic Peninsula have resulted in decreases in UV-B radiation at the surface,[16, 53] opposing the effects due to decreasing total ozone.

Satellite-based trend estimates of UV radiation at the Earth's surface have not been updated during the last four years. Therefore, only changes in UV radiation derived from ground-based measurements and attribution to different factors are discussed in the following.

Time series of UVI in the period 1979–2017, derived from the TUV radiative transfer model[127] are compared with measurements at Arrival Heights, Antarctica, under all-sky conditions (**Fig. 6**). The column amount of atmospheric ozone was the only input parameter allowed

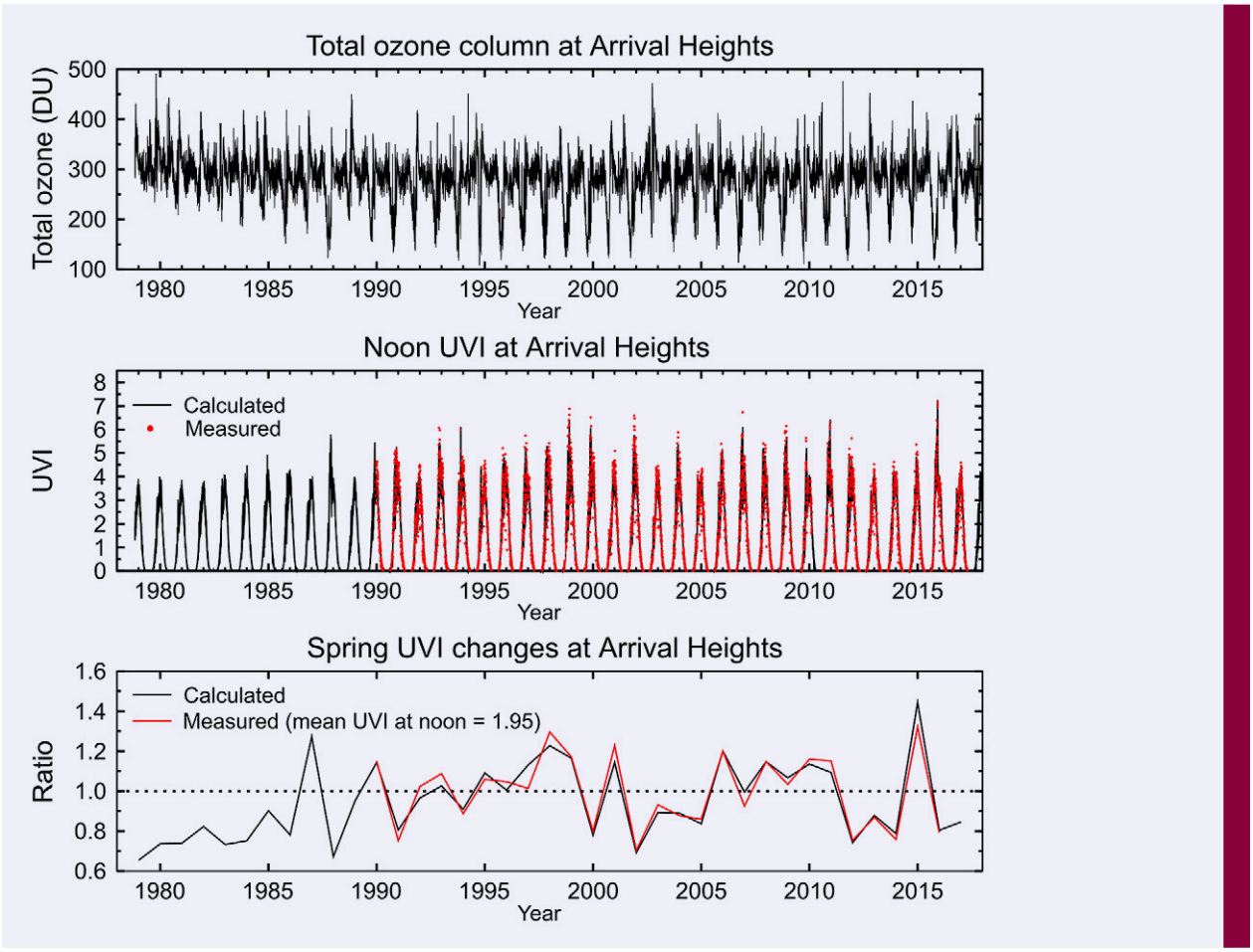

Fig. 6 **(Top panel) Time series of daily total ozone at Arrival Heights (77.8°S, 166.7°E), Antarctica, derived from satellites for the 1979–2017 period. (Middle panel) Time series of daily noon UVI from measurements under all skies and model calculations based only on total ozone data. The measured UVI data (red symbols) are derived from spectra measured close to local noon by a SUV-100 spectroradiometer. Up to 2009, the instrument was part of the NSF UV monitoring network[23] and is now a node in the NOAA Antarctic UV Monitoring Network (https://www.esrl.noaa.gov/gmd/grad/antuv/). (Lower panel) Changes in noon UVI for spring (September–November), relative to the long-term mean over the same season, derived from measurements and model calculations.**

to change in the model, with no account being taken of possible changes in aerosols, or surface albedo. Despite that limitation, the clear-sky envelope of measurements of UVI closely follows the model for the years where both are available. The largest changes in the UVI over this station occurred in the 1980s, when no measurements were available to verify the effects of ozone depletion on UV radiation and to assess the variability of UV radiation during this period. Since the 1990s, there has been high variability in UV radiation, which precludes trend detection. Factors other than ozone (e.g., changes in sea-ice- and snow-cover) may explain the small differences between measurement and model.

Changes in solar UV irradiance at 305 nm (a wavelength strongly affected by ozone absorption) and 325 nm (a wavelength only weakly affected by ozone absorption) have been analyzed to estimate trends in the period 1994–2011 for four northern (59°–71°N) and three southern (55°–69°S) high-latitude locations.[62] Although data from as early as 1990 are available, the first few years were excluded from the trend analysis to minimize the influence from aerosols of the eruption of Mt. Pinatubo in 1991, which reduced stratospheric ozone concentrations in the NH between 1991 and 1993. For the northern sites (59°–71°N), trends of spectral irradiance at 305 nm ranged between –8% and +0.4 per decade. The trend averaged over the four sites is –3.9% per decade and is significant at the 95% confidence level. This negative trend agrees with a statistically-significant upward trend in satellite-derived total ozone of about 1.5% per decade. The corresponding trend of spectral irradiance at 325 nm is –0.4% per decade and is not statistically significant, which is consistent with the absence in observed trends of aerosol optical depth and cloud fraction at the four sites. For the three southern sites (55°–69°S), no significant long-term trends were observed for spectral irradiances at 305 and 325 nm as well as for total ozone, aerosol optical depth, and cloud fraction, throughout the entire period of record.

This study[62] is the first suggesting that statistically significant decreases in UV-B radiation at the Earth's surface over northern high latitudes have occurred in response to the recovery of stratospheric ozone. However, this finding has yet to be confirmed with observations at other locations to become more robust. In general, it is more difficult to detect trends in UV radiation than in total ozone because ozone-related changes in UV radiation are often masked by varying attenuation of UV radiation by clouds, aerosols, and other factors. For example, changes in solar UV radiation observed in northern mid-latitudes during the last two decades have been mainly controlled by clouds and aerosols rather than by ozone.

A study of a 20-year record (1994–2014) of spectrally resolved UV irradiance in Thessaloniki, Greece,[70] revealed increases in annual mean UV irradiance of 2–6% per decade. Updated time series of the anomalies of spectral irradiance at two wavelengths (307.5 nm and 350 nm representative of UV-B and UV-A irradiance, respectively) up to the end of 2017 are shown in **Fig. 7** for cloud-free conditions. In the June-November period, the increases in irradiance are about 5% per decade for UV-B and 2.5% per decade for UV-A radiation and are caused predominantly by decreasing AOD. The greater increase in UV-B radiation is due to slightly decreasing total ozone in this season and the greater effect of decreasing AOD on UV-B radiation compared to UV-A wavelengths. During the last decade of the record (since the mid-2000s), the UV-A irradiance is no longer increasing, despite the continuing decrease of the AOD. This may be due to the weaker effect of aerosols on longer wavelengths. Ozone effects are largely manifested in the short-term (year-to-year) variability of UV irradiance. In another study, the day-to-day variability of noon-time clear-sky UVI at Thessaloniki was found to be influenced more by aerosols than total ozone, even on days with extremely high

total ozone values.[71] These results are consistent with results for other locations discussed previously.[12]

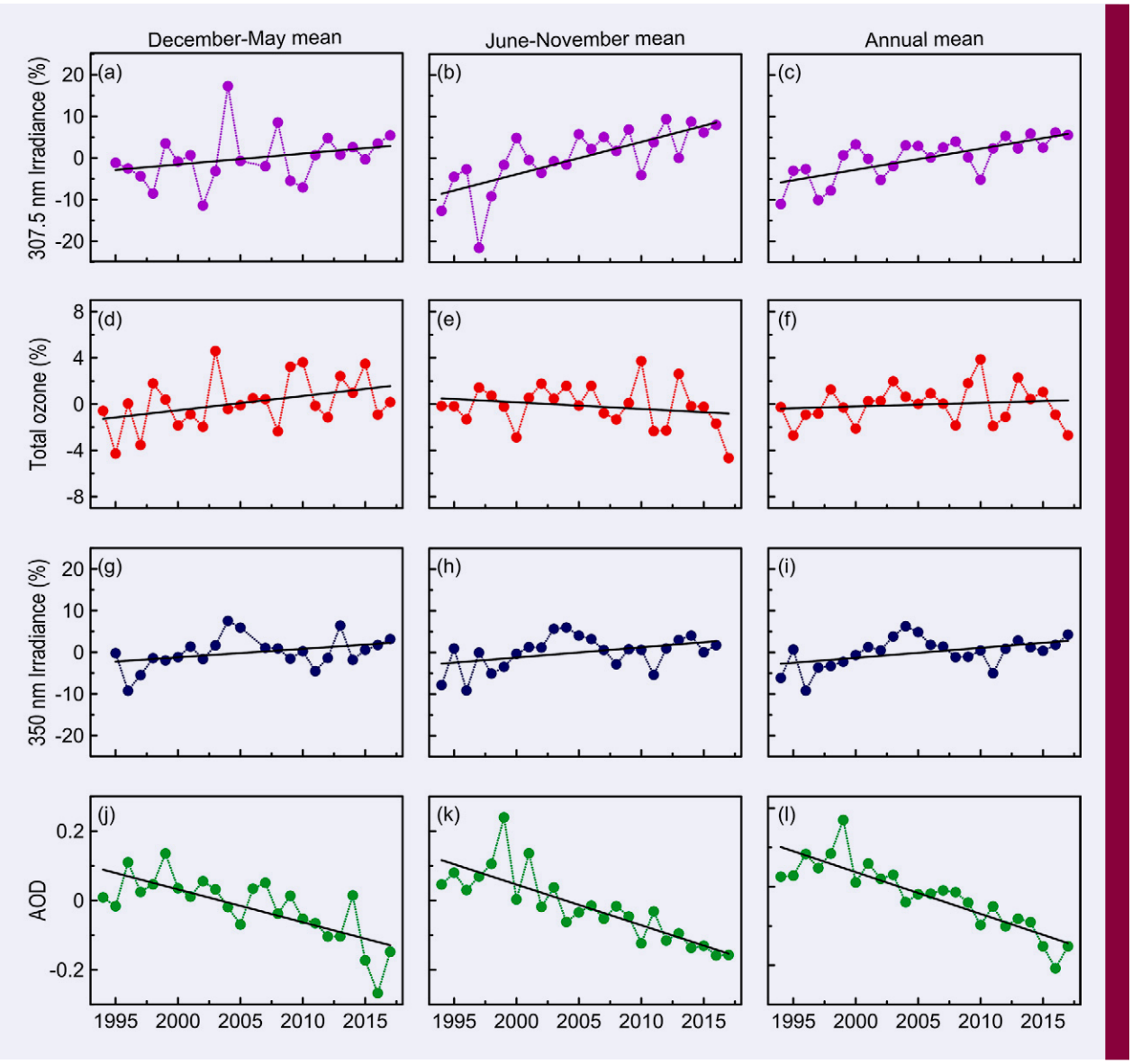

Fig. 7 **Seasonal and yearly mean anomalies in percent relative to the long-term mean for clear sky irradiance at 64° solar zenith angle for 307.5 nm (a, b, c) and 350 nm (g, h, i), total ozone column (d, e, f) and aerosol optical depth at 320 nm (j, k, l) for December–May (left panels), June–November (middle panels) and for the entire year (right panels). The AOD anomalies are expressed in absolute units. Linear trends are shown in each panel (black lines). The figure is adapted from ref.[70] and updated to include data for 2015–2017. Data were recorded at Thessaloniki, Greece.**

Decreasing cloudiness with corresponding increases in UV radiation is part of a larger-scale phenomenon. For example, decreases in cloudiness over Europe have been confirmed with satellite data for the period 1983–2010.[175] According to this analysis, the annually averaged solar irradiance has increased by about 2 W m^{-2} per decade over Central and Eastern Europe. Depending on location, this change corresponds to a 1–2% increase in UV irradiance attributable to changes in cloudiness. At Chilton, United Kingdom (51°N), the variability in the erythemal annual dose has been investigated based on 25 years of data (1991–2015).[89] A large increase of 4.4% per year was found between 1991 and 1995, attributed to effects on total ozone from the eruption of Mt. Pinatubo in 1991 and an increase in total annual sunshine hours over this 4-year period. From 1995 to 2015, the dose decreased at a rate of 0.8% per year, and for the period 2000–2015, the decrease is slightly faster at 1.0% per year. Trends for all periods are significant at the 95% confidence level; however, no ozone measurements were included in that study, so an unambiguous attribution of the observed changes is not possible.

As discussed above, in densely populated or urban areas, changing aerosol effects can mask changes in UV-B radiation that arise from changes in ozone. Despite increasing total ozone over the 1991 to 2013 period, erythemally-weighted irradiance at Uccle, Belgium, increased by 7% per decade due to a combination of decreasing aerosol and cloud amounts, which more than counteracted the effect of ozone.[54] Their statistical analysis showed that trends in UV-B irradiance and total ozone changed in the late 1990s, consistent with the recovery of stratospheric ozone starting at about the same time.

4.3 Reconstruction of past changes in UV radiation from proxy data

Long-term datasets of surface UV radiation from ground-based instruments are sparse and only a few datasets adequately cover the period since the onset of ozone depletion. In the absence of direct measurements, empirical models have been used in combination with total ozone measurements and proxy data to reconstruct past UV irradiance levels. Changes in UV radiation due to clouds are frequently estimated from short-wave irradiance measured with pyranometers or instruments that record sunshine duration. These reconstructions are often limited by the availability of ozone data derived by satellites, which started operating only in the late 1970s. However, total ozone has been measured from the ground at a few research stations starting as early as 1926, and these data have been used to estimate longer-term historical levels of UV radiation.[123]

Two of the longest series of erythemal irradiance dating back to 1964 were reconstructed for two locations in Central Europe; in Belsk (52°N), Poland[167] and in Hradec Králové (50°N), Czech Republic.[48] The reconstruction for Belsk was based on a statistical model using aerosol extinction and total ozone data.[167] Increasing aerosols caused a decline in clear-sky UVI of up to 6% between 1964 and the mid-1970s, while increases in the UVI of about 5–6% per decade in 1974–1996 were caused in equal parts by ozone depletion and decreasing aerosols. Since 1996, monthly-mean UVI at local noon has not changed substantially, as there have been no systematic changes in aerosol concentrations and total ozone over this period.

In Hradek Králové, the time series of erythemal irradiance was reconstructed using a radiative transfer model and additional empirical relationships.[48] Increases in daily doses of erythemal irradiance of up to 15% per decade were found in the 1980s and the 1990s,

which were linked to the steep decline in total ozone of about 10% per decade. In the 1960s, the 1970s and the 2000s, the major driver for the observed changes in daily doses was the change in cloud cover, with mean annual doses in most recent period (2004–2013) declining by about 5%.

UV radiation for the period 1950–2011 was reconstructed from a variety of proxy data for nine locations in Spain.[173] Erythemal irradiance increased over this time by about 13%, of which half was due to decreases in ozone. On a shorter time-scale, 1985–2011, an increase of about 6% was calculated, mostly due to decreasing amounts of aerosols and clouds.

Measured and reconstructed data (using total ozone, snow depth, and daily sunshine duration as proxies) for the Polish Polar Station, Hornsund (77°N), have revealed no statistically significant trend for the period 1983–2016. However, statistically significant decreases in monthly doses of erythemal irradiance of about 1% per year were detected in May and June for the period 1996–2016.[111] This trend could not be attributed to observed increases in total ozone. Instead, cloud cover changes were identified as the main driver of the long-term UV changes at the site.

Statistically significant decreases in daily surface UV radiation from 1961 to 2015 were reported over most regions of China, ranging between 0.27 and 0.63 kJ m^{-2} per year (0.15 and 0.37% per year).[124] These trends were derived from reconstructed data based on a model and proxy data from 724 weather stations, and are caused mainly by changes in aerosols and clouds. Unfortunately, no measurements of UV-B radiation were available at these stations, but trends in UV-B radiation are expected to be at least as large as those for total UV.

In conclusion, these reconstructions confirm that long-term changes in UV radiation over northern mid-latitudes since the onset of stratospheric ozone depletion in the mid-1960s have been mainly caused by changes in aerosols and clouds. Decreasing stratospheric ozone played a role at mid-latitudes only up to the mid-1990s.

5 Projections of UV radiation

Model-derived projections of UV radiation for the future have been extensively discussed over the last decade and presented in previous assessment reports.[214, 216, 217] These projections were based on variables affecting UV radiation which were derived from climate models and were updated as new improved climate models became available. In the following, we summarize new model results that update our assessment of changes in UV radiation for the next few decades and for the end of the 21st century.

Levels of UV-B radiation at the Earth's surface have been influenced by declining total ozone since the 1960s, particularly over the high latitudes of the SH including Antarctica. As concentrations of ODS started decreasing from the late 1990s, factors other than ozone have become the dominant drivers of changes in UV radiation, particularly outside Antarctica. These factors are influenced by increasing concentrations of GHGs and include clouds, aerosols, surface reflectivity, and UV radiation-absorbing air pollutants. Projected levels of UV-B radiation for the future depend on how these factors, including stratospheric ozone, will change in the next decades, and ultimately on the GHG scenario assumed in the respective CCMs.

Several new studies have investigated the dependence of total ozone projections by CCMs forced by different GHG emission scenarios (RCPs),[34, 57, 96, 144] and, subsequently, the dependence of UV radiation projections under clear skies.[34, 144]

Model simulations suggest that stratospheric ozone in the period 2075–2095 will exceed its pre-ozone-depletion (1955–1975) levels at all latitudes outside the tropics, if emissions of CO_2, CH_4 and N_2O continue unabated according to emissions scenario RCP 8.5. All else being equal, this would lead to reduced UV-B radiation over the same time frame.[34] The estimated decreases of noon UVI at northern mid-latitudes in 2075–2095 relative to 1955–1975 range between about 5 and 15%, with the largest decreases projected for the winter months, thus limiting UV radiation available for synthesis of vitamin D during winter even further (see Chapter 2). For the southern mid-latitudes, the estimated decreases in UVI are smaller, ranging between about 3 and 10%. Noon UVI is projected to decrease in the Arctic by up to 20% in spring and to increase in Antarctica by up to 3% at the same season. In contrast, if actual emissions of CO_2, CH_4 and N_2O could be aggressively reduced according to the RCP 2.6 scenario, by the end of the 21st century, UVI would increase relative to the 1960s (in response to slower recovery of ozone than for other RCPs) by up to 5% at all latitudes, except in the spring at high latitudes.[34] In the Arctic spring, noon UVI is projected to decrease by up to 5%, while over Antarctica remaining halocarbons would continue to deplete polar ozone and, together with changes in circulation, would increase the UVI by up to 20%. Note that these projections for UV radiation were based on an approximated relationship between UVI and total ozone, thus have not considered changes in clouds, aerosols, or surface reflectivity. Changes in UV-B radiation due to these factors are expected to be of comparable magnitude with, or in some cases, even greater than those related to changes in ozone.[12]

In another study,[144] simulations with a CCM were forced by three different GHG emission scenarios: RCP 4.5, RCP 6.0 and RCP 8.5. In the tropics, significant increases in DNA-weighted UV radiation by the end of the 21st century relative to the 1960s were found for all scenarios. These increases are driven by the respective projected decreases in total ozone. The largest increases were found for RCP 6.0, reaching 15% in specific tropical regions (e.g., in South America, south Asia and over large parts of the Pacific Ocean). The average increase in DNA-weighted irradiance over the tropics ranges between 1 and 5% for different RCPs. In this study, cloud effects were considered internally in the CCM calculations. Of note, the action spectrum for DNA damage is shifted towards shorter wavelengths compared to the action spectra for erythema. DNA-weighted irradiance is therefore more sensitive to changes in ozone compared to erythemal irradiance quantified with the UVI, resulting in greater changes for the same change in ozone.

In a third study, focusing on the Arctic and northern high latitudes,[69] UV-B radiation is projected to decrease in 2090–2100 relative to 2000–2015 for both the RCP 4.5 and RCP 8.5 scenarios. These projected decreases are due to the recovery of total ozone, increases in cloud cover, and reduction of surface reflectivity caused by the shrinking of sea-ice- and snow-cover. Over land, the greatest reductions are projected for spring (April), under all-sky conditions and for RCP 8.5, locally reaching about 30% for the noon UVI and about 50% for the noon effective dose required to generate vitamin D. For RCP 4.5 these decreases are about 10% smaller than for RCP 8.5.

From these studies, it is evident that projections of UV-B radiation are very sensitive to the assumed scenarios for GHG emissions, which influence all factors that affect UV radiation, including ozone, especially with the recent finding that there has not been universal

compliance to the Montreal Protocol.[147, 228] Furthermore, sensitivity studies with models that participated in the IGAC/SPARC Chemistry-Climate Model Initiative (CCMI) concluded that concentrations of ozone derived from these models are subject to considerable uncertainties arising from the range of anthropogenic forcings specified in these models.[149] In addition, the processes that affect UV radiation and the interactions among the different factors that drive changes in UV radiation are not sufficiently well known. The overall uncertainties in projections of future UV radiation are therefore difficult to quantify.

Our previous assessment report[12] discussed the attribution of projected changes in UVI for the future to changes in total ozone, AOD, surface reflectivity and clouds, whereas the total ozone projections were provided by the CCMval models.[63] In this report, updated estimates of projections for the noon UVI are presented, following the same methodology but based on more recent projections of ozone, reflectivity, and clouds, obtained from the CCMI models.[149] Input data from only four of these models were used[9], because only these provided projections for both total ozone and surface reflectivity. These new model simulations are different from the former CCMval simulations because different scenarios for future concentrations of ODSs and GHGs were used. Projections for the period 1960–2100 were provided by the "REFC$_2$" simulations of the CCMs, which assumed changes in GHGs according to the RCP 6.0 scenario[130] and changes in ODSs according to the A1[225] scenario.[149] Under the RCP 6.0 scenario, total ozone outside the tropics is projected to increase above its historic levels by the end of the 21st century. For RCP 8.5 this increase is larger.[57]

For the aerosol effects on UV radiation, AOD at 550 nm was derived according to RCP 6.0. The average AOD from nine models participating in CMIP5[10] was used.[207] Finally, the effects of clouds were quantified with the cloud modification factor (CMF) that is used to derive the UVI under all-sky conditions from the UVI under clear skies. The CMF was derived from simulations provided by two of the CCMI CCMs (HadGEM3-ES and MRI-ESM1r1) that had data available for the calculation of the CMF. The calculation of the wavelength-dependent effects of aerosols and clouds on UVI follows the methodology of the previous assessment report.[12]

Based on monthly values of these projected variables, the noon UVI under clear skies was calculated for each climate model, using the UVSPEC/libRadtran radiative transfer model.[134] Results are presented for two 10-year periods representing the present decade (2010–2020) and the future (2085–2095). Multi-model average differences in noon UVI for four months are shown in **Fig. 8**. The projected changes in UVI are sensitive to latitude and season, and can be attributed to different factors (ozone, aerosols, surface reflectivity, and clouds) that also exhibit a latitudinal and seasonal variability. The contribution of changes in these factors to the projected changes in UVI is shown in **Table 1** for seven latitude bands and for four months.

9 CCMI models: EMAC-L47MA, EMAC-L90MA, MRI-ESM1r1, HadGEM3-ES

10 CIMIP5 models: CESM1-CAM5, CSIRO-Mk3-6-0, GISS-E2-H, GFDL-ESM2M, HadGEM2-ES, MIROC-ESM-CHEM, IPSL-CM5A-MR, MRI-CGCM3, NorESM1-ME

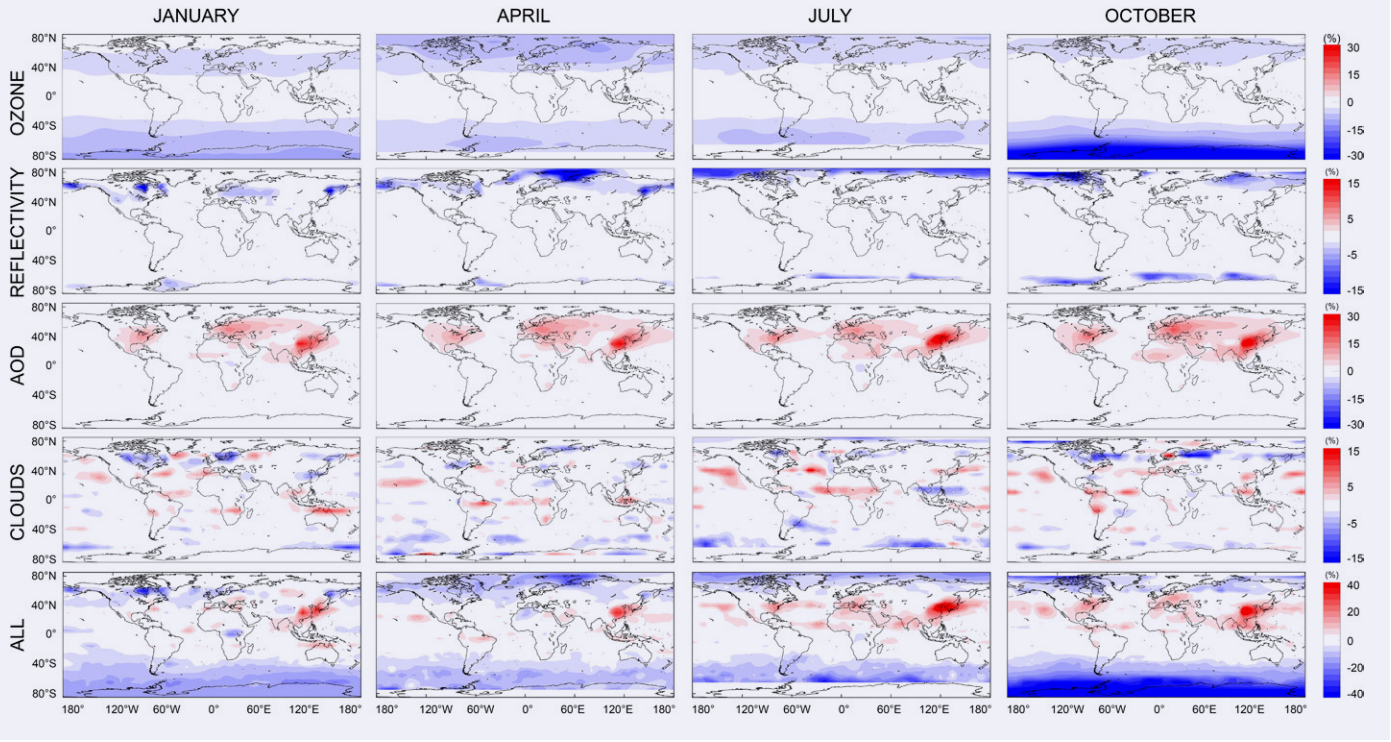

Fig. 8 **Average changes in noon-time UVI calculated from CCMI simulations, between decadal averages for the present day (2010–2020) and at the end of this century (2085–2095; RCP 6.0 scenario) for four months, calculated from projections by CCMs, including effects of changes in ozone, surface reflectivity, aerosols, and clouds. Also shown for each month are individual changes in UVI due to changes in each of these factors, while the others are kept constant. Note that the scale of the color coding is different for each factor.**

Table 1 **Average percentage changes in noon-time UVI calculated from CCMI simulations, between decadal averages for the present day (2010–2020) and at the end of this century (2085–2095; RCP 6.0 scenario), for seven latitude bands and four months. Also shown are contributions to changes in UVI from changes in total ozone, surface reflectivity, aerosol, and clouds. The mean and spread (standard deviation; SD) of the model results from all grid points in each latitude band are shown, as well as the minimum and maximum percentage change in UVI. Data for April and July in south polar latitudes and for January in northern polar latitudes are missing as solar radiation is close to zero in these months.**

		January			April			July			October		
		Avg ± SD	Min	Max	Avg ± SD	Min	Max	Avg ± SD	Min	Max	Avg ± SD	Min	Max
N. Polar	Ozone	POLAR NIGHT			−8 ± 1	−9	−7	−6 ± 0	−6	−5	−3 ± 0	−4	−3
> 80°N	Reflectivity				−3 ± 5	−21	0	−8 ± 3	−11	−1	−7 ± 6	−20	0
	Aerosol				2 ± 0	0	2	−1 ± 1	−2	1	0 ± 1	−1	1
	Clouds				0 ± 0	−1	1	−2 ± 2	−8	2	−3 ± 5	−18	5
	UVI				−9 ± 6	−27	−3	−14 ± 3	−19	−6	−14 ±11	−36	5

		January			April			July			October		
		Avg ± SD	Min	Max	Avg ± SD	Min	Max	Avg ± SD	Min	Max	Avg ± SD	Min	Max
N. High	Ozone	−3 ± 1	−5	−2	−7 ± 1	−9	−5	−5 ± 1	−6	−4	−4 ± 1	−6	−3
60°N–80°N	Reflectivity	−2 ± 3	−16	1	−3 ± 3	−16	0	−1 ± 2	−11	0	−3 ± 3	−17	0
	Aerosol	2 ± 2	0	7	2 ± 2	0	9	1 ± 1	−1	5	2 ± 2	0	10
	Clouds	−1 ± 3	−10	8	0 ± 1	−7	3	0 ± 2	−8	6	−1 ± 4	−16	15
	UVI	−6 ± 8	−35	11	−8 ± 5	−27	2	−5 ± 4	−16	4	−7 ± 5	−22	7
N. Mid	Ozone	−4 ± 1	−6	−1	−5 ± 2	−8	−1	−3 ± 1	−5	−1	−2 ± 1	−4	0
30°N–60°N	Reflectivity	−1 ± 2	−16	1	0 ± 1	−15	0	0 ± 0	−2	0	0 ± 0	−4	0
	Aerosol	4 ± 4	−1	26	5 ± 4	−1	28	5 ± 5	1	38	5 ± 5	1	38
	Clouds	0 ± 2	−10	7	0 ± 1	−6	6	1 ± 2	−4	15	0 ± 2	−10	9
	UVI	0 ± 7	−27	34	−1 ± 6	−17	32	5 ± 8	−6	54	5 ± 7	−8	53
Tropics	Ozone	−1 ± 1	−3	0	0 ± 1	−2	0	−1 ± 1	−3	0	−1 ± 1	−3	0
30°S–30°N	Reflectivity	0 ± 0	0	0	0 ± 0	0	0	0 ± 0	0	0	0 ± 0	0	0
	Aerosol	1 ± 2	−4	19	1 ± 2	−5	21	1 ± 2	−6	16	1 ± 3	−4	21
	Clouds	0 ± 2	−5	12	0 ± 2	−5	12	0 ± 2	−8	8	0 ± 2	−4	11
	UVI	0 ± 4	−19	17	1 ± 3	−8	23	1 ± 3	−8	19	2 ± 4	−8	26
S. Mid	Ozone	−5 ± 2	−8	−2	−4 ± 1	−6	−1	−5 ± 1	−7	−1	−6 ± 3	−12	−1
30°S–60°S	Reflectivity	0 ± 0	0	0	0 ± 0	0	0	0 ± 0	−1	0	0 ± 0	−2	0
	Aerosol	0 ± 0	−1	5	0 ± 0	0	6	0 ± 0	0	5	0 ± 0	−1	5
	Clouds	0 ± 1	−4	4	−1 ± 2	−6	5	−1 ± 2	−9	3	0 ± 1	−3	5
	UVI	−7 ± 3	−14	2	−6 ± 3	−15	3	−7 ± 4	−20	6	−9 ± 5	−21	2
S. High	Ozone	−8 ± 1	−10	−7	−6 ± 1	−7	−5	−6 ± 0	−6	−5	−23 ± 8	−35	−9
60°S–80°S	Reflectivity	−1 ± 1	−5	0	−1 ± 1	−7	1	−2 ± 3	−10	2	−2 ± 3	−12	1
	Aerosol	0 ± 0	−1	0	0 ± 0	0	0	0 ± 0	−1	0	0 ± 0	−1	1
	Clouds	−1 ± 2	−12	2	−1 ± 3	−14	16	−3 ± 3	−12	7	−1 ± 2	−9	3
	UVI	−14 ± 2	−21	−9	−10 ± 4	−31	4	−17 ± 7	−34	−3	−33 ± 8	−48	−14
S. Polar	Ozone	−10 ± 0	−10	−9	POLAR NIGHT						−35 ± 1	−37	−33
> 80°S	Reflectivity	0 ± 0	−2	0							0 ± 0	0	0
	Aerosol	0 ± 0	0	0							0 ± 0	0	0
	Clouds	0 ± 0	0	1							0 ± 1	−1	3
	UVI	−13 ± 1	−15	−12							−44 ± 1	−48	−41

The most important projected changes in UV radiation by the end of the 21st century compared to the present decade are:

(i) the large decreases at high and polar latitudes (> 60°), with UVI values decreasing on average by 33–44% in the SH during spring and by 5–15% in the NH during summer and autumn. These are due mainly to the projected increases in total ozone column and, for the NH, decreases in surface reflectivity.

(ii) the large increases at some northern mid-latitude regions, locally reaching 40% higher UVI values. These increases are due mainly to projected reduction in aerosol optical depth over densely populated and industrialized regions like East Asia, Central Europe and Eastern USA. In some of these areas, decreasing or increasing cloudiness modify the effects of aerosols, leading to enhanced or reduced UV radiation levels.

For the southern polar latitudes, decreases in UVI of about 44% in October and 13% in January are almost entirely due to the projected recovery of stratospheric ozone by the end of the century and the disappearance of the Antarctic ozone 'hole'. The effect of ozone is rather uniform in the entire area, as manifested by the small range of the changes, while the contribution of the other factors is negligible.

For the SH high latitudes, the pattern is similar to the polar region but decreases in UVI are smaller in all months ranging from about 10% in April to 33% in October. In this latitude band the changes in UVI due to changes in reflectivity and clouds become more important, despite the small average values that do not exceed 3% across all seasons. The spread of the changes due to these factors is large, ranging from –12 to +2 for the reflectivity and from –14 to +16% for the clouds. This variability leads to a less uniform pattern of the changes in UVI.

Average projected changes in UVI at SH mid-latitudes are negative and similar across seasons (range –6 to –9%), while their spatial variability is large, ranging between 6 and –21%. Main contributors to these changes are increases in stratospheric ozone (–1 to –12% change in UVI) and changes in cloudiness (–9 to +5% change in UVI). Concentrations of aerosols over the SH at mid-latitudes to the pole are already low; therefore, their effects on average changes in UVI are negligible.

In the tropics, average projected changes in UVI are small (about 1%) for all variables, leading to small average increases of 0–2%. However, the large spread of the effects of aerosols (–6 to +21%) and clouds (–8 to +12%) leads to a large spread of the changes in UVI ranging spatially between –19% and +26%. Considering the large uncertainties in the projections of clouds, the magnitude of this large spatial variability is highly uncertain. However, the tropics include some areas that are projected to have fewer aerosols in the future, such as southeastern Asia, which explains the large projected increases in UVI. The greatest decrease in UVI is projected in January for Central Africa due to projected increase in future aerosols.

At NH mid-latitudes, changes in UVI are dominated by large increases driven by the projected decreases in AOD. Increases in UVI are found for all seasons, locally reaching 54%, while on average the effect is much smaller, close to 5%. The largest increases are projected for China, Europe and Eastern USA, so that the UVI will increase to levels comparable with those at cleaner urban areas at similar latitudes. Reduced concentrations of aerosols have already been observed during the last two decades over urban areas in Europe and Eastern USA (see Chapter 6) At some of these locations, where measurements of UV irradiance were available, the reduced aerosols have led to increases in UV radiation, as discussed in section 4.

The effect of the projected increases in total ozone above the pre-ozone-depletion levels due to increasing GHGs contributes from 0 to –8% to the projected decreases in UVI. Clouds are also important contributors inducing regional positive or negative changes in the UVI in the range –10 to +15%. Finally, in the northernmost mid-latitudes, projected reductions in surface reflectivity in January and April lead to decreases in UVI of up to 16%, particularly over areas presently covered by sea ice or snow, which are projected to decrease dramatically in the future (e.g., Sea of Okhotsk, Russia, and Alaska).

At NH high latitudes, projected increases in ozone have similar effects to those at NH mid-latitudes. Reduction in surface reflectivity across all months is the dominant factor for the projected average decreases in UVI of about 6%. The large spatial variability of projected surface reflectivity and cloudiness which, as noted above, are associated with large uncertainties, lead to a very large spread in the projected changes in UVI ranging from –35 to +11%. The effects of changes in aerosol in this region are small, leading to average increases in UVI of less than 2%.

Finally, at the polar latitudes of the Arctic, the UVI is projected to decrease by the end of the 21st century relative to the present, on average by about 9% in April and about 14% in July and October. Regional changes in UVI of –36 to +5% are projected due to projected increases in total ozone (effect on UVI: –9 to –3%), decreases in reflectivity (effect on UVI: 0 to –21%), and changes in cloudiness with effects on UVI of –18 to +5%.

The estimated changes in the UVI between the present decade and the end of the 21st century are associated with large uncertainties arising from the uncertainties of the projections of all factors, in addition to the effect of the assumed RCP scenario, which was discussed above. We estimate up to 30% uncertainty in the UVI calculations due to uncertainty in the aerosols, and particularly in the SSA. Variations of projections of different CCMs are also important. For April and July, only 50% of the projected changes in UVI over all latitudes are larger than the corresponding inter-model standard deviation. This percentage is even smaller (about 30%) for January and October. Therefore, our confidence in these estimates for the future is low (especially given the possible non-compliance issues discussed earlier). However, these estimates represent our best knowledge for the projected levels of UV radiation at the Earth's surface that are currently available. For regions and seasons where the projected changes in UVI are large (e.g., greater than 5%) at least the direction of the changes is more certain.

The conclusions from the new UVI simulations do not substantially change our understanding of the projected changes in UVI by the end of the century relative to the present decade, as discussed in the previous assessment, where we found that UV is expected to increase in the tropics, where it is already too high for optimum health; and to decrease elsewhere, where it is sometimes too low for optimum health.[12] The magnitude of changes is somewhat smaller, owing to differences in the projections of the factors affecting the surface UV radiation, and the scenarios considered for their changes in the future. The latter is probably the most important source of the uncertainties for the UV radiation projections.

6 Implications of geoengineering for UV radiation

Solar Radiation Management (SRM) (also known as "geoengineering") has been suggested for counteracting the warming from increasing GHG by reducing the amount of solar radiation absorbed by the Earth's surface. Proposals for SRM include space reflectors, increasing of marine clouds, and injection of sulfuric aerosols into the stratosphere.[30, 52] Since then, several studies have discussed potential implications of such actions for the atmosphere and the biosphere, including side effects on stratospheric ozone and solar UV radiation.[25, 98, 217, 226] Impacts on stratospheric ozone would occur through: (i) chemical effects of the increased aerosol loading, (ii) resulting changes in temperature and scattered solar radiation in the stratosphere, with corresponding changes photolysis rates, both of which will impact the ozone chemistry, and (iii) resulting changes in stratospheric circulation and transport. Recent studies have concluded that, despite progress in understanding the potential environmental, political, and societal risks and benefits of solar geoengineering, the current state of knowledge remains insufficient for conducting a comprehensive assessment that would be required for making future decisions on deployment.[107, 126, 171] Here we assess only effects of geoengineering on UV radiation. A more comprehensive discussion is included in the report of the Science Assessment Panel.[228]

Increased concentrations of sulfate aerosols from the continuous injection of SO_2 into the tropical stratosphere would have an effect similar to that from large volcanic eruptions. Model simulations of such solar geoengineering actions estimate losses in stratospheric ozone in most latitudes, which would lead to increases in UV-B radiation at the surface. However, the additional aerosol in the stratosphere would decrease UV radiation (both UV-B and UV-A) and increase the proportion of diffuse to direct solar radiation due to increased scattering by the aerosols.[165, 210] Such increased diffuse radiation may influence the growth of plants since diffuse radiation is received and absorbed more effectively than direct radiation (see ref.[118] and Chapter 3) The estimated mean increase of diffuse radiation averaged over the UV-visible range (300–700 nm) is 11%.[231] However, because of commensurate losses in the direct beam component, the increase in global radiation (direct plus diffuse) would be smaller. Exposure of humans and ecosystems to enhanced UV-B diffuse radiation could have many important implications (as discussed above and detailed in Chapters 2–4.

7 Advances in UV monitoring and modeling

In this section we discuss advancements in measuring UV radiation from the ground and space, as well as methods to determine personal exposure. Advancements in instrumentation to measure aerosol properties have been discussed in sections 3.2.

7.1 Ground based systems

UV radiation at the Earth's surface has historically been measured with scanning spectroradiometers, broad-band instruments with a response function mimicking the erythemal response, and multi-filter instruments, which measure the spectral irradiance at several wavelengths (typically 4–7) in the UV range.[217] Spectroradiometers using double-monochromators are the most accurate instruments because of their ability to suppress stray light from the visible range that would otherwise be detected as wavelengths in the UV-B.

In the past, the quality of spectral UV measurements has been assessed with intercomparison campaigns, which bring together instruments from various networks to perform measurements side by side that are subsequently analyzed. In 2015 and 2017 two such campaigns were organized in the framework of the EUBREWNET COST action ES1207 (http://rbcce.aemet.es/eubrewnet) in El Arenosillo, Spain, with participation of more than 20 Brewer spectrophotometers.[169] An intercomparison campaign of erythemal detectors took place in summer 2017 at PMOD/WRC in Davos Switzerland.[92] Finally, three spectroradiometers representing different networks in Australia and New Zealand took part in a two-month campaign in Melbourne, Australia, in autumn 2013.[77]

The alternative to these campaigns is the use of a reference instrument that is transported to UV monitoring locations, to operate synchronously and be compared with the local instrument(s). In the early 2000s, a portable reference spectroradiometer known as QASUME (Quality Assurance of Spectral solar UV Measurements in Europe) was developed and has performed more than 65 site visits to 33 European stations since 2001.[93] A comprehensive analysis of the instrument's uncertainties has recently been completed and a new reference spectroradiometer, named QASUMEII, was constructed, taking advantage of improvements in measuring techniques during the last decade.[93] For example, QASUMEII uses a hybrid detection system, which combines the high sensitivity of a UV-optimized photo counter with the good stability of silicon photodiodes. For wavelengths between 310 and 400 nm and SZAs smaller than 75°, measurement uncertainties at the 95% confidence level are 3.08% and 2.02% for QASUME and QASUMEII, respectively. Compared to QASUME's uncertainty of between 4.6% and 8.8%, depending on SZA, assessed in 2005,[80] improvements implemented during the last decade have reduced the instrument's uncertainty by more than half.

Despite their advantages in terms of measurement accuracy, scanning spectroradiometers are expensive to procure and operate, and scan-rates are comparatively slow. It may take more than 10 minutes to measure a spectrum in the UV range,[93] which makes it difficult to assess the effects of fast changes in intensity, for example, due to moving clouds. During the last decade, array spectroradiometers (ASRMs) have been increasingly introduced for spectral irradiance measurements in the UV. These instruments typically use a charge-coupled device (CCD) detector, which records the entire UV spectrum within seconds. However, for physical reasons they cannot use double-dispersion as with scanning spectroradiometers, and measurement errors caused by insufficient suppression of stray light typically limit the useful spectral range of these devices to wavelengths longer than about 305 nm, in particular for large SZAs.[77] For example, in 2014, solar measurements of 14 commercially available ASRMs were compared against QASUME during a campaign in Switzerland.[61] Almost all instruments applied a state-of-the-art numerical stray light correction.[151] Despite this correction, almost all measurements were affected by stray light at wavelengths shorter than 310 nm and overestimated the global spectral irradiance below this wavelength for all SZAs. However, some well-characterized instruments were able to determine the UVI to within 5% of QASUME measurements for SZAs less than 50°. For larger SZAs, the measurement accuracy deteriorated for all ASRMs participating in this campaign.

Recently, a radiometer was introduced that uses an array spectroradiometer in combination with several interference filters mounted in a filter wheel to reduce the effect of stray light.[244] A comparison of data from this instrument against a research grade spectroradiometer showed agreement within 10% for wavelengths larger than about 305 nm.[243]

We conclude from these results that the accuracy of currently available ASRMs is not sufficient to detect and quantify the small changes in surface UV radiation expected at mid-

latitude locations caused by ozone depletion and, eventually, by ozone recovery. However, the instruments are useful for monitoring the spectrum of radiation in situations when the radiation field changes rapidly (e.g., partly cloudy conditions or under tree canopies). ASRMs have been widely used to study the effects of solar UV-B radiation in terrestrial ecosystems.[26]

Lack of proper quality control of data from radiometers of any type can lead to erroneous data and false conclusions, as for example the extremely high UVI of 43.3 at the tropical Andes reported by Cabrol *et al.*[35] A recent study where the data and methods were critically reviewed and incorrect data were identified, suggests that the maximum UVI at this location was in the range of 25 ± 5.[140]

The number of stations with high-quality spectral UV measurements is currently declining[11] and future funding for many of the remaining stations is uncertain.[227] If this trend continues, the scientific community may lose the ability to assess changes of UV radiation at the Earth's surface and associated impacts, to verify satellite UV data with ground-based observations, and to validate model projections.

7.2 Satellite validation

UV radiation at the ground has been estimated from measurements of various space-borne sensors since the late 1970s.[86, 205] These estimates are derived from backscattered radiances measured by the sensors in combination with radiative transfer model calculations. Uncertainties of these estimates are typically larger than for direct measurements at the surface because not all model parameters can be adequately quantified from space. For example, absorbing aerosols in the boundary layer are difficult to detect by satellites.[6] In general, sensors on satellites can provide reliable estimates of surface UV irradiance under low-aerosol and clear-sky conditions, but these estimates may be affected by large systematic biases over polluted areas, under overcast skies, or above snow-covered surfaces, as discussed in more detail in the following.

Irradiance estimates are generally less accurate for UV-B than UV-A regions of the spectrum. For example, the irradiance inferred from the Ozone Monitoring Instrument (OMI) onboard NASA's Aura solar-stationary satellite exceeded clear-sky ground-based measurements at Thessaloniki, Greece, by up to 14% at 305 nm and up to 10% at 310 nm. In contrast, at 324 nm and 380 nm, the OMI data underestimated the UV irradiance by less than 5%.[236] These wavelength-dependent biases indicate that the spectral absorption and scattering properties of aerosols are not correctly addressed by the satellite data-retrieval algorithm.

Comparisons between OMI UV data and ground-based measurements at 13 stations located in the Arctic and Scandinavia from 60°N to 83°N revealed large biases due to incomplete knowledge of the surface albedo.[20] When the surface albedo is known, OMI data typically exceed ground-based measurements by 0–11%. Otherwise, biases are much larger, ranging between +55%, when the albedo assumed by OMI is too high, to –59% when it is too low. These large negative biases are observed when reflections from snow and ice, which ultimately increase downwelling UV irradiance, are misinterpreted as reflections from clouds.

At the Observatoire de Haute Provence (OHP), located in a pristine mountainous region of southeast France, UV data from OMI and the Global Ozone Monitoring Experiment (GOME-2) overestimate the clear-sky noon-time UVI relative to ground-based measurements by only

11 http://www.montreal30.io3c.org/sites/montreal30.io3c.org/files/pictures/20%20matin/Braathen-WMO-GAW-Ozone-UV.pdf

6% and 2%, respectively. At Saint-Denis (SDR), another pristine site located on La Réunion Island in the Indian Ocean, both OMI and GOME-2 observations are biased high by 4% relative to ground-based observations. These small biases generally increase for all-sky conditions and are 9% at OHP and 11% at SDR.[28]

A new dataset of UVI observations with broadband instruments at six locations in South Africa recently became available.[36] Time records at four of the six sites are as long as 21 years. For clear-sky days, the mean bias between ground-based and OMI measurements at the time of the satellite overpass is less than ± 0.6 units of UVI.

At Hoboken, New Jersey, USA, UVI values reported by OMI agree to within ±2% with ground-based measurements with a NILU-UV multifilter radiometer for clear-sky conditions.[64] With increasing cloud cover, OMI overestimates the UVI at the surface, reaching 24% on average for overcast conditions.

UV data products provided by the Tropospheric Emission Monitoring Internet Service (TEMIS) were recently compared with ground-based measurements at Thessaloniki, a moderately polluted site in northern Greece.[237] TEMIS UV data were derived from total ozone measurements provided by the SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY (SCIAMACHY) up to April 2012 and are based on GOME-2 for later years. Cloud attenuation over Europe is provided by several Spinning Enhanced Visible and InfraRed Imagers (SEVIRI). Because SEVIRI instruments are installed on geostationary satellites, TEMIS data products take changes in cloud cover throughout the day into account, in contrast to OMI UV data, which are based on observations of clouds at the time that the earth rotates under the satellite. For cloud-free days, the bias between erythemal daily doses from TEMIS and ground-based measurements at Thessaloniki is less than ±2%. For all-sky conditions, TEMIS overestimates ground observations by 12.5%. Similar positive biases with increasing cloudiness were also reported.[28, 64] At highly polluted locations such as Santiago, Chile, satellites may overestimate the UVI at the Earth's surface by up to 47% on average.[217]

Observations of instantaneous total ozone and erythemal irradiance for the entire sunlit globe commenced in June 2015 using data from the Earth Polychromatic Imaging Camera (EPIC) installed on board the Deep Space Climate Observatory (DSCOVR), which is located at the Lagrange Point L1 between the Earth and sun.[85] At L1, the satellite rotates synchronously with the Earth about the sun due to the concurrent action of the gravitational forces of Earth and sun. At this point of equilibrium, DSCOVR is "parked" at a near constant distance of about 1.6 million kilometers from Earth. This vantage point allows unique observations of the sunlit globe from sunrise to sunset that are performed multiple times per day as the Earth rotates in EPIC's field of view. Neither geostationary nor low Earth-orbiting satellites such as OMI can produce similar data or images. Retrieved ozone amounts agree with ground-based measurements and satellite data to within 3%. It has been demonstrated that erythemal irradiance can be calculated from this instrument's data at a nadir resolution of 18 × 18 km^2. These new measurements confirm previous results from satellite data[121] and from ground-based instruments[42, 50, 141, 235] that the highest UVI on Earth of greater than 20 occurs in Peru, Bolivia, and Chile at high elevations of the Andes Mountains during summer months (**Fig. 9**). Solar radiation is less attenuated when reaching such high-altitude locations, compared to sea-level, due to smaller amounts of atmospheric molecules in the column above, resulting in extreme values of the UVI.

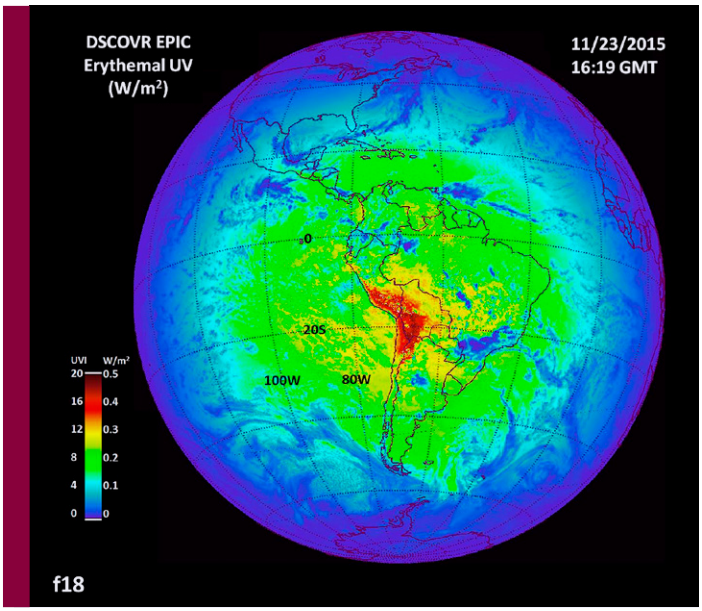

Fig. 9 **UVI data over South America derived from DSCOVR on 23 November 2015 at 16:19 UTC. Extremely high values are shown in the Andes Mountains in Peru, Bolivia, and Chile corresponding to a UVI greater than 20. Local solar noon is at 64.75°W and sun is overhead near 20°S. (Adapted from Herman *et al.*[85])**

UV data from satellite instruments are often provided at a spatial resolution of tens of kilometers. A method has been proposed to scale the UVI data provided by the space-borne Ozone Monitoring Instrument (OMI) down to 1 × 1 km² grid. This downscaling was achieved by interpolation of satellite data and other measurements (e.g., surface albedo, aerosol optical depth, cloud cover, dew point, ozone, surface incoming shortwave flux, and sulfur dioxide).[220] Such higher resolution data can be more useful in studies where UV radiation data at specific locations are needed.

By combining ozone data from GOME-2 and cloud data from AVHRR/3 satellite sensors, an improved algorithm was developed to estimate different biological weightings of surface UV radiation, as well as UV-B and UVA, at 0.5° spatial resolution.[112] New global erythemal dose datasets were constructed from OMI measurements and are provided at 0.25° spatial resolution (about 25 km at the equator).[16] Both datasets can be useful for large-scale ecological studies, presuming that possible mismatches between the provided biological weightings and the weighting of interest, as well as the target geometries (e.g., human body or tree shapes), are properly taken into account.

Spectral irradiance is derived from satellite data using, among others, information of the reflectivity of the Earth's surface below. Recent field experiments indicated that when soot, volcanic sand, and glacial silt are deposited on a surface covered by snow, they sink within minutes into the snow. For reflected radiation measured by satellite radiometers at nadir viewing directions (i.e., vertically below the satellite) the surface appears darker, but for larger viewing angles it appears brighter, almost as reflective as the natural pristine snow.[161] These discrepancies in the estimated reflectivity may affect the accuracy of satellite-derived spectral irradiance data over snow-covered regions. Ground-based measurements of UV radiation are not prone to this error.

7.3 Personal exposure

The highest-quality measurements of UV radiation from ground-based spectroradiometers are not generally applicable to understanding personal exposure. Firstly, these instruments are generally positioned in locations that are not typical of every-day exposure. Secondly, they typically measure the cosine-weighted irradiance received by a horizontal surface. To more realistically model personal exposure, information on the directional distribution of radiation (radiance) from all directions (i.e., including downwelling and upwelling radiance from the upper and the lower hemisphere, respectively) would be preferable. However, such measurements are not widely available.[182]

For example, the exposure of the human body to UV radiation was calculated with a radiative transfer model by integrating incident radiation over the 3D geometry of the body.[177] When this approach is applied for a snow-free valley and for snow-covered mountain terrain (with albedo of 0.6), an increase in UV exposure by 10% per 100 m increase in altitude was found, which is more than 10 times larger than the usual increase in erythemally weighted UV irradiance with altitude in snow-free conditions.[12, 138] The results imply that upwelling radiation is an important source of exposure to UV radiation affecting human health where exposure occurs at higher altitudes (see Chapter 2).

A new modelling tool (SimUVEx v2),[170] allows the evaluation of the contribution of the direct, diffuse, and reflected components of UV radiation for different sizes of shade structure. According to this study, although shading can lead to decreases in exposure to direct UV radiation greater than 97% for the upper body areas, such as the head and the neck, a large fraction of the diffuse UV radiation is always present. For example, a subject without adequate protection under a sun umbrella would receive sufficient diffuse radiation for inducing sunburn in 2 hours (12:00–14:00) in the summer.

The radiation field incident on a person is usually obstructed by buildings or trees, including man-made canyons from buildings that reduce the sky view, and can reduce UV amounts appreciably.[39, 87] Even if direct sunlight is not obscured, reductions in erythemally-weighted radiation can be substantial because usually at least 50% of unimpeded radiation would be from diffuse skylight. For the same reason, protection from the direct beam alone without obstructing a significant fraction of skylight cannot afford substantial protection from UV radiation. For example, the vitamin D_3-weighted UV exposure of a human with vertical posture was calculated for urban locations to investigate the impact of the orientation of obstructions on the exposure.[178] It was found that, at the spring equinox at a mid-latitude site in Germany, the exposure of a human model with winter clothing in an environment where obstructions cover 40% of the sky varies by up to 25%, depending on the orientation of the human model to the sun. It was also found that for these conditions, the accumulated vitamin D_3-weighted exposure of a human with winter clothing walking during the lunch break is reduced 40% by obstructions from buildings and vegetation.

Total personal exposure also depends critically on the amount of time spent outdoors. On a typical summer's day, the ambient UV dose can exceed 70 SED[12],[136] which corresponds to more than 30 MEDs for fair skinned individuals if they are exposed to sunlight throughout the day with no protection. But generally, personal exposure times to sunlight will be much shorter. They are also highly variable from person to person (Chapter 2), as well as with time and location.

While electronic UV dosimeters can be difficult to use and are more expensive than traditional dosimeters (e.g., spore[185] or polysulfone[191] dosimeters), they have several advantages: firstly, electronic dosimeters can be tuned to more closely match the biological weighting of interest than is the case for polysulfone dosimeters, for which differences between their response function and action spectrum of interest can be large.[40] Secondly, even if there are significant differences between the instrument response and the target weighting, the latter can still be derived from the measurements using radiative transfer models that include ozone and SZA as inputs. This is generally not possible for the older dosimeters because of their long integration periods that include a wide range of SZA.[184] Thirdly, the time series of data from

12 SED or Standard Erythemal Dose equals 100 J m^{-2} of erythemally-weighted UV irradiance, which quantifies the effect of UV radiation in the development of sunburn.

the electronic dosimeters can assist in quality assurance and in verifying compliance of the users to the measurement protocols. For example, if the dosimeter is not actually worn, but left stationary, that can be obvious from the data record. Finally, accuracy will generally be improved from the reusable dosimeters, which generally have a linear response compared with the less precise logarithmic response of older dosimeters. Nevertheless, the accuracy of these devices is still not comparable with that of research-grade spectroradiometers.[180]

Since the last assessment report,[217] there has been some progress in the use of electronic and other types of dosimeters in measuring the exposure to UV radiation in a wide variety of conditions. These include the general public during clinical trials in New Zealand to determine the relationship between UV exposure and vitamin D,[179] members of an Antarctic expedition,[174] high school students in Switzerland,[81] seafarers working on decks of vessels,[66] skiers in Italy,[41] tennis players in Spain,[184] hikers in Spain and France,[184] and runners.[158, 184] Dosimeters measure the UV dose at the site where the dosimeter is worn (lapel, wrist, etc.), and will have a biological effect only on the fraction of the unprotected skin exposed. For example, skiers expose a small fraction of their body in contrast to swimmers. In most cases, the personal dose was only a small proportion of the available ambient UV dose. The mean exposure for the general public in New Zealand[179] and of students in Switzerland[81] was less than 2% of the ambient dose. The Swiss students received 85% of their cumulative UV dose on weekends and holidays. For outdoor sporting activities, their doses were larger. Measurements with polysulfone detectors showed that skiers in Italy would receive 65% of the ambient dose on average to any exposed skin. The median daily UV exposure of hikers and tennis players typically exceeded 5 SED, according to one study, with maximum exposures being much higher. A recent review of 55 studies on Non-Occupational Personal Solar UV Exposure measurements suggests that knowledge on exposure of humans to UV radiation has clearly increased, especially in the past decade.[176]

The solar UV radiation environment relevant to recreational boaters on oceans was simulated with radiative transfer models that take scattering and absorption processes in the atmosphere and the ocean into account.[60, 145] UVI values were calculated for horizontal (pertinent for a sunbather on a boat) and vertical orientation (approximating the face and trunk of an upright person standing on a boat deck), assuming a total ozone column of 332 DU. For overhead sun, the UVI on a horizontal surface was 13.6 with approximately equal contributions from the direct and diffuse components, while the upwelling irradiance (corresponding to lying prone with the considered body surface, such as the head, over the side of the boat) was 0.7 or 5% of the downwelling UV radiation. This indicates that contributions from reflections of the ocean surface and radiation emanating from the ocean (i.e., the water-leaving radiance) are only minor contributors to erythemal irradiance at the sea surface. For a vertical surface, the UV dose rate depends critically on the SZA and its orientation relative to the sun and is obviously highest when facing the sun in azimuth. When facing away from the sun, the surface-reflected contribution is about 16% of the total, showing that radiation originating from below the horizon contributes only little to sunburn at sea.

The studies by Diffey and Mobley and Mobley and Diffey[60, 145] also suggest that swimming in the ocean provides little protection from exposure to the sun. Even for depths as large as one meter below the surface, the UVI can be comparable with that at the surface. For example, depending on chlorophyll concentrations (c_{chl}), the UVI one meter below the surface is reduced to about 87%, 85%, and 50% for c_{chl} = 0.05, 1, and 5 mg m^{-3}, respectively. However, the study did not consider attenuation by dissolved organic matter (DOM, see Chapter 4) and particulates, and therefore overestimates the UVI at depth for coastal locations.

7.4 Low-cost, crowd-sourcing sensors (smart phone applications)

The main determinant of personal UV exposure is the time spent outdoors without protection. So, any tool that would help people reduce excess exposure will be beneficial. Forecasts of the peak UVI at any point on the globe are currently available from Google maps (e.g., http://sunburnmap.com).

New tools are becoming available for monitoring sun exposure. Different approaches include electronic UV dosimeters, films with photosensors that are applied to the skin, and smartphone apps with or without photosensors, or linked devices.

Smartphones offer potential as personal monitors of exposure to solar UV radiation. A low-cost hand-held UVI meter combined with smartphone applications provided accurate estimates of UVI and the duration of the solar exposure to receive 1 MED.[82] Another option is the use of smartphones for UV radiation 'nowcasting'. The UVI derived from this system showed a better match with observations at the site of sunbathing, compared with 24 h forecasts of UV radiation using atmospheric models.[83]

An English and Spanish search in App Store and Google Play Store found 134 apps designed to improve sunscreen use, of which 88 were in English only. The location-based UVI was given in 64 apps, and 16 also informed the user about appropriate sunscreen use.[208] Randomized controlled trials have used smartphone apps that deliver sun protection advice, such as information on the UVI, sun protection strategies, alerts to apply sunscreen, and when to get out of the sun.[31] These interventions resulted in modest improvements in sun-protection behaviour, such as increased use of shade and wide-brimmed hats.[31]

A smartphone app for Android devices has recently been introduced for Poland,[82] providing estimates of the current UVI and duration of skin exposure to get 1 MED. Although there are several smartphone apps that are designed to advise the public about UV risk, few have been validated.[32, 82] Their accuracy depends mainly on their ability to forecast changes in ozone, clouds, and aerosols. The relative importance and variability of these three factors can vary widely from place to place, so validation at multiple sites is required.

Images from smartphone cameras have been tested as UV monitoring devices for improved personalization and public awareness of exposure to UV radiation. Currently the accuracy of these devices is much lower than scientific-grade UV sensors in use, either due to poor technical characteristics and calibration,[97] or due to inappropriate measurement principles.[143]

In the last few years, the possibility of using smartphones to record radiation spectra has emerged, mostly by coupling various classes of entrance optics to these units with data recording achieved using the smartphone camera. UV spectra recorded with these devices have been based on sensors located outside of the smartphone body. However, as some smartphone manufacturers already use UV transmitting optics (e.g., a sapphire lens on the iPhone) and others monochrome sensors (e.g., on some Huawei units), direct recording of UV spectra with smartphones may become a reality in future.[135] These UV spectra could be weighted with the relevant action spectrum to determine the biologically effective UV for a variety of processes, e.g., in terms of the action spectrum (up to 330 nm) for previtamin D_3 synthesis,[27] and the erythema action spectrum.[47] As has already been illustrated with the iSPEX project,[192] this sort of hardware has great promise for widespread proliferation to broaden current monitoring data, particularly in concert with the citizen science community.

Another recent development is the use of wearable UV-sensitive patches that determine personal exposure from changes in patch colour. Sunscreen can be applied to the patch, which has been designed to have the mechanical properties of skin. Changes in colour can be imaged with a smartphone app which, after skin type input, can indicate a "safe" exposure, set at 0.4 MED. Of note, MED increases with skin type on average, but skin type alone does not predict MED on an individual basis. Thus, there may still be a risk of excessive sun exposure for more sensitive skins. While these are in the early stages of development and use, their low unit cost and automated logging via phone networks provides the capability to record UV exposure from large numbers of the general public in everyday settings.[5, 190] As such, they show great promise for epidemiological studies. Data from the latter study show high geographical variability in exposure patterns, and large differences between the patterns of personal exposure and ambient UV radiation. In the USA for example, measured personal UV doses in Oregon and Minnesota were much greater than in New Mexico, Texas, or Florida, despite much lower ambient UV in the northern states. Such differences may be expected, in this case, due to deliberate sun-avoidance in the hot conditions. However, the population subsets may not be widely representative (see Chapter 2).

Data from such devices should be used with caution for information on actual sun-burning radiation levels, but may be helpful in public health campaigns, pending further evaluation.

8 Action spectra for effects on humans

This section discusses the implications of imprecise knowledge of action spectra for the estimation of effects of UV radiation on humans. Spectral dependence of UV effects on ecosystem processes, such as photosynthesis, viral survival and dissolved organic matter degradation are considered in Chapters 3–5).

8.1 Action spectrum for damage to skin

The action spectrum for melanoma in humans is still not known. Instead, inferences on risks are usually made from erythemally-weighted irradiances, assuming the action spectrum for the induction of skin cancer is similar.

In a recent study, the need for blocking of infrared radiation (IR) in sunscreens has been questioned.[58] Some sunscreens incorporate agents that are said to protect against IR damage in the skin. However, evidence for their benefit in the context of normal human behaviour in the sun is lacking. The paper examined typical IR exposure levels to the sun and industrial sources to decide whether there is a need for sunscreens to contain IR-blocking agents. They found that lifetime levels of IR exposure resulting from typical behaviour in the sun are less than those experienced by workers exposed to industrial sources of IR, such as steel and glass furnaces. Yet these workers appear to suffer little in the way of chronic skin damage. The authors concluded that there is no compelling evidence for including IR blockers. Based on this finding, it appears that any IR component of erythema must be small. However, more work in this area would be valuable.

Another study investigated the reasons for sunscreen protection factors determined in the laboratory appearing higher than those determined in natural sunlight.[59] The authors proposed that the discrepancy could be explained if the erythema action spectrum were extrapolated beyond its current limit of 400 nm into the visible, where the component from sunlight is much larger than in the lamps used to test the products in the laboratory.

A corollary of this would be that erythema would depend more on the full spectrum of solar irradiance, rather than being dominated by the UV-B component. If that were the case, erythemal irradiance would be less dependent on ozone than previously assumed, and the radiation amplification factor for ozone changes would be smaller than the currently used values of about 1.1. This would reduce the importance of changes in atmospheric ozone as a driver of skin damage. The magnitude of the difference would depend on the weighting at longer wavelengths.

8.2 Action spectrum for synthesis of vitamin D

Recent work has suggested limitations to the present action spectrum for synthesis of pre-vitamin D_3, and a possible need for its revision. As has been noted in recent reports,[12, 157] the currently-used CIE action spectrum for synthesis of pre-vitamin D_3 in human skin[27] may not be correct and may also change as a function of exposure. A recent paper discussing chemical modelling of the full set of complex reaction pathways in vitamin D photo-synthesis involved in skin chemistry predicts an initial action spectrum that is similar to the CIE action spectrum, but is displaced to shorter wavelengths.[218] Such a displacement would be more consistent with the observation that little vitamin D is produced at latitudes poleward of 40° in winter.[83] Further, this work provides evidence that the shape of the vitamin D action spectrum changes as a function of exposure to UV radiation and will become negative at wavelengths between 315 and 330 nm after exposures of only a few SED. A negative action spectrum means that pre-vitamin D_3 is destroyed rather than produced after absorption of photons in this wavelength range (**Fig. 10**). If true, this would have important implications for people who are confined indoors behind glass windows, which transmit only UV-A, but not UV-B radiation. Continued exposure to sunlight through glass windows could even be detrimental to vitamin D status. The study by van Dijk *et al.*[218] also highlighted large differences in the absolute amounts of vitamin D derived by the various action spectra for

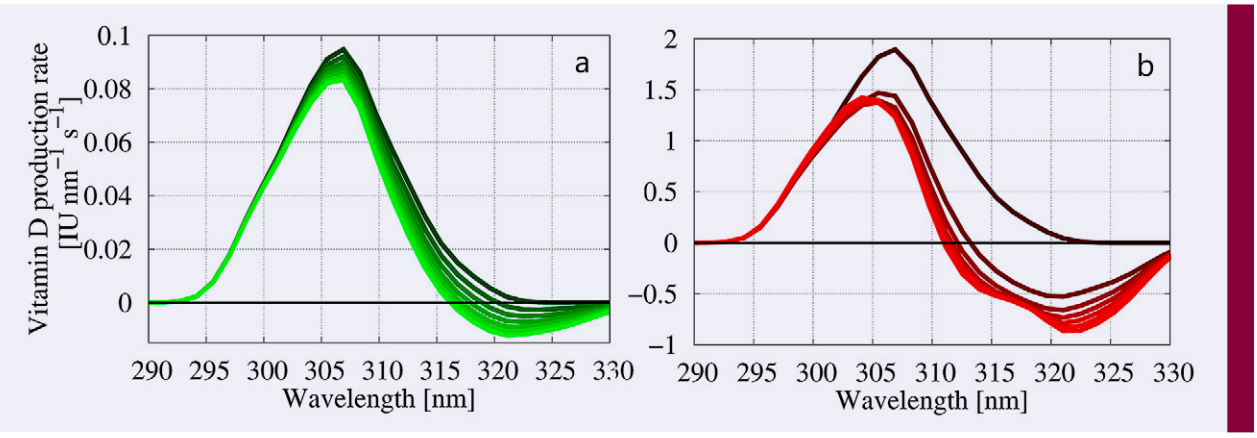

Fig. 10 **The decline of synthesis of vitamin D (and partly reversal into destruction) due to the formation of other photoactive compounds in the skin, as discussed by van Dijk *et al.*[218]. The plots show the deduced spectral production rates for synthesis pre-vitamin D3 for skin in the lower back/upper leg, for SZA = 30°. Spectra are presented for different stages of exposure, ranging from 0 SED (darkest) to 7.5 SED (brightest). Plot-a is based on an action spectrum from the authors' group at RIVM and Plot-b is based on an action spectrum from a group at the Queensland University of Technology (QUT). Results between these two differ by a factor of about 20.**

vitamin D that are currently proposed by the two groups involved. The reason for this factor-of-20 difference is not understood at present, and it highlights a lack of understanding in the photo-synthesis of vitamin D. The action spectrum that is currently recommended by the CIE,[27] is intermediate between the two discussed, and in the absence of further evidence, we recommend its continued usage, despite its obvious limitations.

8.3 Action spectrum for phototherapy of psoriasis

Psoriasis is a skin disease that is treated by phototherapy, including sunlight-exposure (i.e., heliotherapy). The action spectrum for clearance of this condition is similar to that for erythema, but with stronger wavelength dependence. An analytic representation of the action spectrum has been developed.[110] A subsequent publication[109] showed that the effective radiation for psoriasis treatment can be estimated from the more widely available erythemally-weighted UV irradiance database. They reported that successful anti-psoriatic heliotherapy would require exposures of 2–3 hours at UVI values of 3–4. Unfortunately, this exposure period is much longer than the maximum time recommended to avoid skin damage (erythema). For example, erythemal damage occurs after exposure times around 1 hour at UVI = 3 in individuals with Fitzpatrick skin-type II. Further work is needed to evaluate the effectiveness of this treatment, and whether the health benefits outweigh the potentially harmful effects. The action spectrum currently used was derived from a small number of measurements made in the 1980s. More detailed knowledge of the action spectrum is needed, because small errors in it would lead to large errors in calculating the doses of sunlight required for effective treatment.

8.4 Risk-Benefit analyses

Risk-benefit assessments from exposures to UV radiation are usually based only on the action spectra for erythema (sun-burning) and synthesis of vitamin D.[138] In the light of the above findings, calculations of risk-benefit thresholds from exposure to UV radiation may require revision.

In practice, no broad-band detector can perfectly match the biological response (e.g., erythema, synthesis of vitamin D, psoriasis treatment, etc.) of interest. For meaningful quantitative results, corrections that are functions of ozone and SZA must be applied to measurements with these detectors. However, such corrections have not always been applied in the literature, and without them, the relevance of the UV measurement data is questionable.

Errors also arise from the use of UV irradiance data incident on a horizontal plane, rather than on the surface of interest. There can be appreciable differences between these two quantities. In the case of effects on humans, their attire, posture, and time spent outdoors are also required.

9 Gaps in Knowledge

According to[228] and the discussion above, the full recovery of the ozone layer in the mid and high latitudes of the SH will take several decades. It is therefore essential to continue long-term monitoring of total ozone and UV radiation at the Earth's surface without degrading the quality of data.[227] It is concerning that the number of active monitoring stations is declining worldwide, particularly in view of the recently-discovered new emissions of CFC-11.[65, 147]

The effects of changes in stratospheric ozone on the UV radiation received at the Earth's surface can be estimated with a very good degree of accuracy. In contrast, and despite progress in recent years, it is still difficult to account for the interactive effects of clouds and aerosols. Over areas with high surface reflectivity (snow- or ice-covered areas) the relevant processes are even more complicated. The estimate of future UV radiation levels is uncertain because of the assumptions in defining the development of these variables over time. All these variables will be affected by anthropogenic changes in GHGs and other species, such as the ODSs. Better understanding of the contribution of changes in ozone and GHGs to changes in the SH climate would improve predictability of climatic characteristics, such as the variability of atmospheric circulation cells, sea ice, winds, precipitation, and clouds.

Aerosols over the highly polluted areas of south-eastern Asia and China will dominate changes in UV radiation at these locations in the future. However, these changes depend on the amount and optical properties of aerosols (including the wavelength dependence of their absorption efficiency) both in the present and the future. There are still large uncertainties in quantifying the SSA of aerosols and its wavelength dependence, despite recent new studies that have contributed to our understanding.

Improvement in the understanding of these processes and the availability of higher quality information on the interaction of these factors with UV radiation would strengthen our ability to effectively interpret ongoing projected changes in UV radiation. More accurate projections of UV radiation are essential for accurately assessing effects on human health, ecosystems, materials and related services. Furthermore, quantification of economic and societal impacts resulting either from the projected changes in UV-B radiation or from the avoided changes due to the successful implementation of the Montreal Protocol is still missing.

Concerning the accuracy in estimating biological and health effects of UV radiation, there is incomplete knowledge of the action spectrum for erythema, especially for wavelengths beyond 400 nm in the visible (and possibly IR) regions of the spectrum, as well as of the action spectrum for pre-vitamin D_3. A full understanding of the differences in the action spectra for the various types of skin cancer in humans is also still lacking but will be difficult to obtain.

To more realistically model personal exposure, information on the directional distribution of radiation (radiance) from all directions (i.e., including downwelling and upwelling radiance from the upper and the lower hemisphere, respectively) would be preferable. However, such measurements are not widely available.

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2 Human health in relation to exposure to solar ultraviolet radiation under changing stratospheric ozone and climate

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Summary

Due to the success of the Montreal Protocol, there have been only small increases in UV-B (280–315 nm) radiation at the Earth's surface. Thus, increases (and decreases) in human exposure to UV radiation have been due mainly to changing behaviour, driven by sociocultural norms that have altered markedly over the last century. However, observed trends in health outcomes, for example, increasing skin cancer incidence, provide an indication of the potential consequences for human health of changes in stratospheric ozone that increase UV-B radiation at the Earth's surface.

Exposure of the skin to UV radiation is the main environmental risk factor for skin cancers (including melanoma, keratinocyte cancer and Merkel cell carcinoma) and inflammatory conditions of the skin (collectively termed photodermatoses). Since the 1980s the incidence

of skin cancers has increased dramatically in all Caucasian populations. Skin cancer is the most common (e.g., over 90,000 new skin cancers in New Zealand predicted for 2018, compared to *ca* 3000 cases of colon cancer) and most expensive cancer in some developed countries with predominantly light-skinned populations. Incidence trends are now flattening or even reversing in populations where public health campaigns to reduce sun exposure began early, possibly because of concern about stratospheric ozone depletion.

Exposure to UV radiation increases the risk of diseases of the eye including pterygium, cataract and, possibly, age-related macular degeneration. Cataract is the leading cause of impaired vision worldwide (12.6 million blind and 52.6 million visually impaired due to cataract in 2015), particularly in low-income countries where access to cataract surgery is limited. In contrast, reduced time outdoors is associated with an increased risk of myopia, suggesting a possible beneficial role for exposure to UV radiation.

UV-induced immune suppression can result in the reactivation of latent viral infections, potentiate skin cancers caused by viruses such as certain human papilloma virus, and increase risks of bacterial and protozoal infections. Conversely, UV-induced immune suppression can have benefits in the skin in reducing the symptoms of immune disorders such as psoriasis. Furthermore, downregulation of systemic immune responses may reduce the risks of autoimmune diseases including inflammatory bowel disease and multiple sclerosis. Exposure to UV radiation can cause phototoxic reactions associated with commonly used drugs.

The most widely accepted benefit of exposure to UV radiation is synthesis of vitamin D in the skin. While there is consensus that a blood concentration of 25-hydroxyvitamin D (25(OH)D) of < 25 nmol L^{-1} increases the risk of rickets and osteomalacia, controversy remains over whether concentrations higher than this improve bone health. There is little convincing evidence that vitamin D supplementation is beneficial for health except to manage vitamin D deficiency.

It is difficult to compare the prevalence of vitamin D deficiency between locations or over time due to the lack of consensus over the definition of deficiency and historic inaccuracies in measurement of 25(OH)D concentration. However, several studies that have used standardised methods indicate that 25(OH)D < 50 nmol L^{-1} is common in many parts of the world; for example, in a study from Europe the yearly mean prevalence of 25(OH)D < 50 nmol L^{-1} was 40% (and 13% for a yearly mean 25(OH)D concentration of < 30 nmol L^{-1}).

The health risks of sun exposure can be mitigated through appropriate sun protection. New developments include a garment protection factor that reflects both the UV protection factor of the fabric as well as the skin coverage of the garment. New testing is being carried out of sunglasses to ensure that they remain sun-protective at the stated protection factor throughout their typical life. There has been a drive to have higher UV-A (315–400 nm) protection in sunscreens at the expense of UV-B protection for a given sun protection factor, but it is not clear if this has benefits for health.

Use of sunscreen can reduce the risk of skin cancers but may have adverse effects, such as triggering contact and photocontact allergy, typically manifesting as acute dermatitis. There are increasing concerns about sunscreens that wash into the environment, and the possible impacts on aquatic ecosystems.

While there are considerable concerns about the health consequences of interactions between exposure to UV radiation and other factors that will change as a result of climate change, e.g.,

increasing temperature, there is little evidence available currently on which to make firm conclusions of the likely risks.

There are several gaps in our knowledge that require attention, particularly around the balance of risks and benefits of sun exposure in both qualitative and quantitative terms, as well as in relation to sun protection, public health messaging, and future climate scenarios.

1 Introduction

Recognition of and action on depletion of stratospheric ozone occurred against a background of rapidly increasing incidence of skin cancer in light-skinned populations. These increases pre-dated ozone depletion, and resulted from changes in sociocultural norms for clothing, and perceived value of tanned rather than pale skin as a sign of health and affluence.[6–8] Because of actions taken under the Montreal Protocol and its amendments to limit release of ozone depleting substances (ODSs) to the atmosphere, there have not been large increases in UV-B radiation over populated areas of the Earth's surface (reviewed in ref.[25]). Nevertheless, it remains important to recognise the very large potential risks to human health that could be caused by stratospheric ozone depletion. Several analyses of the 'world avoided' by the Montreal Protocol,[237, 249] or predictions of skin cancer incidence under scenarios of runaway ozone depletion,[328, 355, 362] show the scale of these risks.

Future projections, assuming continuing compliance with the Montreal Protocol and its amendments, and dependent on global climate change, are that, by the end of the 21st century, indicate likely 'super recovery' of the global ozone column compared to 1980 levels; and lower ambient UV-B radiation particularly at higher latitudes, due to increased cloud cover. Levels of UV-B radiation may increase in the tropics (depending on the emission scenario modelled), particularly over currently highly polluted areas, as air pollution diminishes.[25] Here we assess the evidence, primarily published since our 2014 assessment,[209] of the risks and benefits to human health of exposure to UV radiation. **Fig. 1** provides a conceptual overview of the Chapter. Biologically relevant exposure to UV radiation (or the dose) depends on behaviour (time in the sun and the amount of the skin exposed) as well as the intensity of ambient UV radiation. To date, increases in exposure have largely occurred due to changes in behaviour, but these provide an indication of the consequences for human health of exposure to higher (and, in the future, lower) levels of UV radiation because of depletion of stratospheric ozone and future recovery.

Recognition of the risks to health from increasing exposure to UV radiation have generated new industries in sun protection. We thus also assess recent progress in sun protection aimed at reducing the effects of exposure to UV radiation to the skin and eyes. The unintended environmental consequences of sun protection, such as sunscreen washing into surface waters, are addressed in Chapter 4. The potential adverse and beneficial effects for health of exposure to chemicals that are transformed into more toxic or less toxic compounds following absorption of UV radiation, e.g., photosensitisation, are discussed in Chapter 5. The potential risks to health from ozone-depleting chemicals and their replacements, and the health burden caused by UV-induced changes in air quality, are discussed in Chapter 6. Other indirect effects on human health are the result of changes in food quality and quantity, and ecosystem services, such as disinfection of surface waters used for drinking, and the

UV-induced degradation of pollutants. These are addressed in Chapters 3, 4, and 5 as are the interactive impacts of climate change for such services.

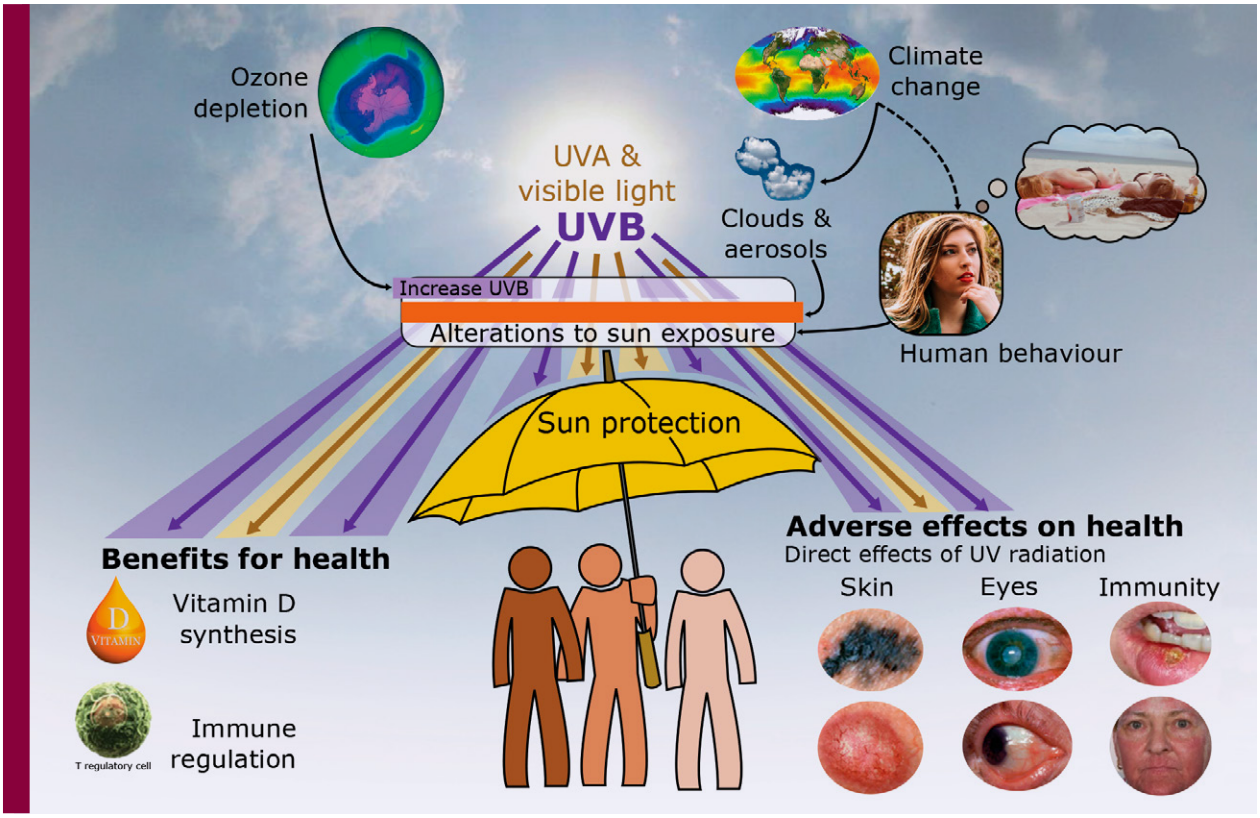

Fig. 1 **Conceptual diagram. Depletion of stratospheric ozone causes an increase in UV-B radiation at the Earth's surface; in the future, recovery of the ozone layer will lead to a reduction in clear-sky UV-B radiation. Climate change will alter cloud cover and tropospheric air quality (aerosols) that will, in turn, affect solar radiation at the Earth's surface across all wavelengths. Human behaviour is a major modulator of the received dose of UV radiation. These factors thus work together to determine human exposure to UV radiation; the dose of UV radiation reaching sensitive tissues depends, in turn, on skin pigmentation and the use of sun protection including physical protections like sun umbrellas, as well as clothing, hats, sunscreen and shade. Adverse effects on health include skin cancers and photosensitivity disorders (photodermatoses), cataracts and other eye diseases, and immune suppression that leads to the reactivation of latent virus infections. Benefits include synthesis of vitamin D in the skin, regulation of immune function that may reduce the severity of some skin diseases and possibly systemic autoimmune diseases. Climate change will alter these risks and benefits to health through changing behaviour in relation to sun exposure, e.g., due to changes in ambient temperature and precipitation. The photograph of the thinking woman in Figure 1 was adapted from an image by Tyler Nix on https://unsplash.com/collections**

In this Chapter, we first present the evidence on the importance of behaviour as a major modifier of the personal received dose of UV radiation, compared to the available ambient UV radiation. We then briefly describe the damage to DNA and modulation of immune function that occurs following exposure to UV radiation that drives both adverse and beneficial effects. This is followed by an assessment of recent research on the adverse effects of exposure to solar UV radiation, beginning with effects on the skin, particularly skin cancers and

photodermatoses, and followed by effects on the eyes, and then emerging evidence on other health risks. The evidence for beneficial effects of UV radiation, including through vitamin D and non-vitamin D pathways is then assessed, followed by a brief consideration of the balance of risks and benefits of sun exposure for health. In the next sections we consider sun protection tools and messaging. We finish with an assessment of recent evidence on possible future effects, including those that may be influenced by climate change (or where changes in UV radiation could influence the health impacts of climate change), and identify some gaps in our knowledge to guide future research.

2 The role of behaviour in determining exposure to UV radiation

Almost 90% of the world's population lives at a location where the peak annual UV Index (UVI) reaches more than 10;[390] thus, the potential for exposure to UV radiation is high. However, the actual personal dose received depends on behaviour. In most locations that have been studied, the mean daily exposure to UV radiation for both adults and children is around 4–5% of the available ambient dose of UV radiation for the day.[131, 133] There is, however, considerable variability,[25] with a range from one-tenth to ten times the mean,[125] highlighting the important role of behaviour. Achieving accurate and personalised measurement of exposure to UV radiation is thus important in individual-level studies of health risks and benefits. Most studies have been undertaken in Caucasian populations and the findings may not be applicable to other ethnic groups.[176] Understanding how exposure to UV radiation may affect health is challenging because there is no definition of an "optimal" exposure. Indeed, it is likely that optimal exposure will be highly variable, according to individual sensitivity, for example, based on genetic factors including skin type, and possibly other factors such as age.

2.1 Changing behaviour in relation to sun exposure under concurrent global environmental changes

There are very few data on the effect of warmer temperatures on patterns of sun exposure. An older study showed that people were more likely to spend at least 15 minutes outdoors on warmer compared to cooler days, but this pattern reversed when outdoor temperatures were > 28°C.[90] More recently, it was found that people living in cooler (but not hotter) climates increased their time outdoors in warmer weather.[383] These data suggest that a simple correlation between rising temperatures and time outdoors is unlikely. It will be important to also consider the effects of urbanisation, including the urban 'heat island' effect, with evidence showing reduced exposure to UV radiation in the man-made canyons typical of cities,[25] as well as changes in cloud and precipitation that reduce the amount of ambient UV radiation, or the time outdoors, respectively.

3 Biological pathways underpinning the effects of exposure to UV radiation on health

UV radiation striking the skin is absorbed by molecules – chromophores – in the epidermis (most superficial layer of the skin) and dermis (below the epidermis). The most energetic,

short wavelength UV-B photons penetrate only into the epidermis and upper dermis, while UV-A photons can reach the deeper dermis. Exposure to UV radiation results in natural adaptation to provide protection through tanning and thickening of the epidermis (epidermal hyperplasia).[80] Darker skin pigmentation is the result of a greater melanin content in the epidermis; this modifies the dose of UV radiation received by epidermal and dermal chromophores (reviewed in ref.[114]; see also section 7.4).

3.1 The importance of DNA photodamage

DNA is a major epidermal chromophore for UV-B radiation (see **Fig. 2**). The cyclobutane pyrimidine dimer (CPD) is the most frequent DNA photoproduct.[52] CPD formation can lead to characteristic mutations – 'UV signature' mutations (C to T, CC to TT) – that are found in cutaneous malignant melanomas (CMMs), keratinocyte cancers (KCs, formerly called non-melanoma skin cancers, and including squamous cell and basal cell carcinoma (SCC and BCC, respectively)), and actinic keratoses (scaly growths on the skin that may be a premalignant stage of SCC). In addition, recent work shows that sun-exposed, but normal-appearing, skin has thousands of clones of abnormal cells, with a high proportion containing cancer-causing mutations.[219] These mutated epidermal cells are actively eliminated by non-mutated cells to restore the normal skin architecture.[47] Skin cancers occur when repair and/or control mechanisms are overwhelmed; skin cancers have more mutations than any other cancer.[62] UV-B and UV-A radiation also cause oxidative damage to DNA and other biomolecules[52] that may contribute to skin cancer genesis.

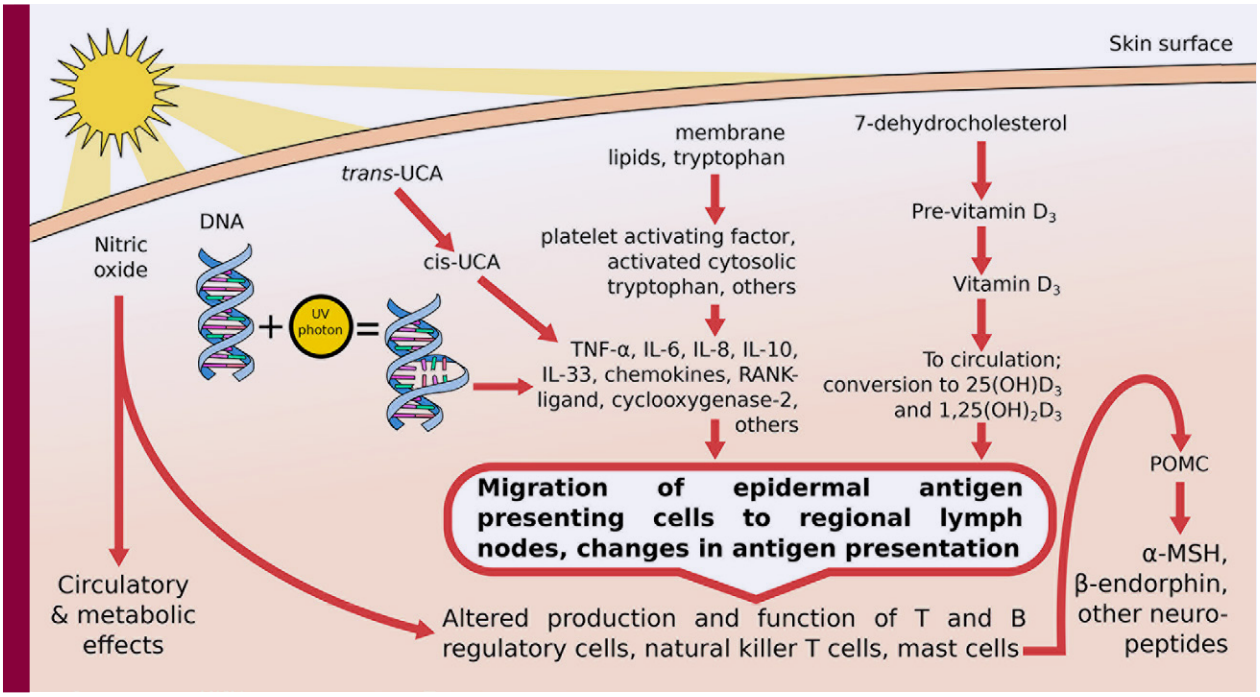

Fig. 2 **Cascading consequences of UV irradiation of human skin. UV photons are absorbed by a range of chromophores, including DNA, membrane lipids, urocanic acid (UCA), and 7-dehydrocholesterol, with subsequent effects on immune cells and secretion of neuropeptides, including α-melanocyte stimulating hormone (MSH). POMC: pro-opiomelanocortin; IL: interleukin; TNF: tumour necrosis factor; RANK: receptor activator of nuclear factor kappa-B.**

3.2 UV-induced modulation of immune function

The human immune system has innate and adaptive (or acquired) components, with considerable communication between them. Innate immune responses are typically rapid[116] while, for those of the adaptive immune system, there is a lag of hours or days between exposure to a pathogen or antigen and the maximal immune response. Both innate and adaptive responses have immunological 'memory'. The 'trained immunity' of the innate system is non-specific but provides short-term (days to months) protection against secondary infection with related or unrelated pathogens.[137, 248] In contrast, immunological memory in the adaptive system is pathogen- or antigen-specific and lasts for years; a subsequent exposure to the same pathogen results in a more immediate, targeted, immune attack.

Exposure of the skin or eyes to UV radiation causes modulation of immune function through pathways that are both vitamin D-dependent and independent. In simple terms, innate immune function is upregulated and adaptive immune function downregulated. Figure 2 provides an overview of events occurring in the epidermis and dermis following UV irradiation that have consequences for immune function. Additional information is provided in the supplementary material.

3.2.1 Upregulation of innate immunity

Exposure of the skin to UV radiation results in the release of pro-inflammatory cytokines (signalling molecules regulating immunity), chemokines (molecules inducing directed chemotaxis), and anti-microbial peptides (AMPs; for a review of AMPs, see ref.[32]). The AMPs can be directly cytotoxic to pathogens and/or facilitate the cytotoxicity of natural killer cells and other cells of the innate immune system.[269]

3.2.2 Suppression of adaptive immunity

UV photons are absorbed by chromophores in the skin. These include DNA, RNA, trans-urocanic acid (UCA), and membrane lipids, including 7-dehydrocholesterol, the precursor of vitamin D. Through a range of pathways this results in upregulation of regulatory T (T_{reg}) and B (Breg) cells, and dampening of cell-mediated immune processes.[148]

4 Adverse effects on human health from exposure to UV radiation

Adverse effects on health from exposure to UV radiation arise from UV-induced immune suppression and damage to the skin and eyes that is beyond the repair capabilities of the body.

4.1 Adverse effects of UV-induced immune modulation

Suppression of immune responses provides a permissive environment for the activation of viral infections and possibly for new bacterial and protozoal infections, impairment of vaccination, the development of skin cancers (see section 4.2.1), and the expression of some photodermatoses (see section 4.2.2).

4.1.1 Activation of viral infections

Several recent studies show an increased risk of reactivation of latent herpes virus infections following exposure to high doses of solar UV radiation. For example, there was a three-fold greater risk of recurrent infection of the eye with herpes simplex virus in association with spending eight or more hours per week outdoors when the UVI was > 4 compared to less time outdoors with UVI < 4.[211] Studies from South Korea,[171] Taiwan,[381] and Australia,[182] show that shingles, caused by the reactivation of herpes zoster virus, is more common when ambient levels of UV radiation are higher (e.g., 10% higher in summer than winter in South Korea[171]).

The human herpes virus, HHV8, is a necessary, but not sufficient, cause of Kaposi sarcoma, a cutaneous malignancy.[63] A study in the USA has shown that in male veterans infected with human immunodeficiency virus (HIV), the risk of Kaposi sarcoma was increased in men who lived in locations with high ambient UV radiation or who had KC prior to the development of Kaposi sarcoma.[53] Other studies describe both positive[132] and inverse[3] associations between levels of ambient UV radiation and the incidence of oral, pharyngeal, and cervical cancers. The positive association was hypothesised to be due to the increased risk of infection with human papillomavirus (HPV, see section 4.2.1 and supplementary material) because of higher exposure to UV radiation. A possible protective effect of vitamin D (see section 5.1) was suggested to explain the inverse association.

4.1.2 Vaccination

The evidence suggesting that exposure to solar UV radiation reduces the efficacy of vaccines, including those against poliovirus, influenza, tuberculosis, measles, and hepatitis B virus, was reviewed in 2011.[252] Since then few investigations in this important area have been carried out. In a systematic review of 24 randomised trials, the effectiveness of Bacille Calmette Guerin (BCG) vaccine against tuberculosis (TB) was progressively higher with increasing distance from the Equator,[217] possibly due to lower UV-induced suppression of immune function at higher latitudes.

4.1.3 Intracellular bacterial and protozoal infections

The lesions of post kala-azar leishmaniasis, a long-term outcome of visceral leishmaniasis, which is caused by a protozoal infection spread by sandflies, occur on sun-exposed body surfaces, suggesting that UV-induced immune suppression may play a key role.[239]

There is conflicting evidence on whether exposure to UV radiation is beneficial or harmful for TB. In a study in Birmingham, UK, notifications for TB were 24% higher in summer than winter,[181] consistent with UV-induced immune suppression. However, a global ecological study reported that the incidence of TB over the period 2004–2013 was 78% lower in countries in the highest quartile of solar UV-B radiation compared to those in the lowest quartile (after adjustment for average pigmentation of skin, degree of urbanisation, consumption of fish, prevalence of type-2 diabetes, and index ranking of human development).[41] In this model, variation in UV-B radiation accounted for 6.3% of the global variation in the incidence of TB. A similar finding of an inverse association between levels of solar radiation and incidence, hospital admissions, and mortality for TB has been recently reported from Chile.[27] The protective effect of higher UV-B or solar radiation was ascribed to higher vitamin D status in sunnier locations as well as upregulation of innate immunity. However, recent studies confirm previous reports that randomised controlled trials of vitamin D supplementation

in people with TB are not effective in reducing signs of infection (sputum smear or culture positivity).[350, 382] The explanation for the inconsistent findings in relation to higher ambient UV radiation is not clear.

4.2 Adverse effects of higher exposure to UV radiation on skin

Exposure to UV radiation that is inappropriately high for the individual's skin type causes sunburn. This ranges from a short-lived mild reddening of the skin, to painful blistering that lasts several days. Other inflammatory reactions of the skin (photodermatoses) occur in people who are abnormally sensitive to UV radiation (see section 4.2.2). Long-term exposure to UV radiation damages the structural proteins in the dermis (e.g., elastin and collagens), causing wrinkling and the typical appearance of photoageing, and is the major environmental risk factor for several types of skin cancer.

4.2.1 UV-induced skin cancers

Skin cancers occur as a result of repeated DNA damage following exposure to UV radiation, incomplete or deficient DNA repair, and UV-induced suppression of acquired immunity. Skin cancer is the most common cancer in populations of predominantly light-skinned people. For example, in New Zealand there are *ca* 3000 new cases of colorectal cancer per year, compared to over 90,000 new cases of skin cancer predicted for 2018.[329] The incidence has been increasing steadily through much of the 20th and 21st centuries. This increase reflects changes in the prevalence of risk factors (e.g., increased leisure time in sunny locations, migration of fair-skinned populations to regions with high ambient UV radiation, changing fashions in clothing, and use of sunbeds), coupled with increased surveillance, early detection, and improvements in tools and criteria for diagnosis.

The two main types of skin cancer, CMM and KC, arise from epidermal melanocytes and keratinocytes, respectively. Merkel cell carcinoma is a much less common skin cancer, which may also be etiologically linked to exposure to UV radiation.

Cutaneous malignant melanoma. Exposure to solar UV radiation is the most important known environmental cause of CMM,[259] typically on a background of phenotypic susceptibility, including lightly pigmented skin, and red or light-coloured hair. A recent study from Canada found that increases of one standard deviation in summer ambient UV radiation were associated with a statistically significant 22% greater risk (hazard ratio = 1.22, 95% CI 1.19–1.25) for CMM.[273] Approximately 5–10% of CMM occur in those with a family history of CMM.[276]

Aetiology: environmental risk factors. In light-skinned populations, estimates of the proportion of risk of CMM that can be attributed to exposure to UV radiation vary from 60%[259] to 96%.[15] A recent assessment of the global burden of CMM attributable to UV radiation estimated that 168,000 new CMMs in 2012 were attributable to 'excess' UV radiation (that is, in comparison with an historic population with minimal exposure to UV radiation), as a result of population changes in lifestyle, from sun avoidance to sun-seeking behaviour.[15] The divergent (dual) pathways hypothesis[373] posits that CMMs can be separated into those that are associated with a high number of naevi (moles), occur in younger people and on typically sun-protected skin, such as the trunk; and those developing on chronically sun-exposed skin,

for example the head and neck, in typically older people with an average number of naevi. Epidemiological evidence strongly supports an increased risk of CMM in association with high-dose intermittent sun exposure (e.g., leading to sunburn) in naevus-prone individuals, as well as a role for chronic sun exposure for some types of CMM; e.g., lentigo maligna melanoma.[14]

Occupational exposure to UV radiation can increase the risk of CMM. A study estimated that, in Britain, there were 241 new CMM in 2011 and 48 deaths from CMM (95% CI 33–64) in 2012 that could be attributed to occupational exposure to solar radiation (particularly in construction, agriculture, defence, and land transport).[298] From 2005 to 2014, CMM was the most frequently diagnosed cancer in active members of the USA military (excluding KC). Incidence rates increased with each additional year of service; for infantry, the incidence at 20 years of service was more than 44 times greater than in the first three years of service (5.34 in year 20 compared to 0.12 average over years one to three, per 10,000 people per year).[48] The equivalent increase for healthcare workers (i.e., primarily indoor occupations) was from 0.50 to 2.82 per 10,000, a 5-fold increase.

High-dose sun exposure at any time during life increases the risk of CMM, but exposure occurring in childhood, and associated with the development of naevi, may be particularly important.[140] A previous report that higher sun exposure prior to diagnosis of CMM was associated with a reduction in subsequent mortality[36] was not confirmed in a more recent study with a rigorous study design and focus on this specific question.[172]

Aetiology: phenotypic risk factors. Having a skin phenotype of higher susceptibility to sunburn (lighter skin or eye colour) was associated with increased risk of invasive CMM among both White and non-White (excluding African American) population groups in the USA Multi-ethnic Cohort Study.[266] The effect was stronger within the non-White than the White group. Incidence of CMM is higher in women than men in the pubescent and reproductive ages in both White and non-White populations.[388] Whether this is the result of a preference for a tan, hormonal influences, or other factors, requires further investigation.

A melanoma risk prediction model incorporating only age, gender, and host phenotypic risk factors (hair, eye, and skin colour, freckling, number of moles), predicted the risk of CMM with 72% accuracy; adding hours of tanning (but not total sunburns), and *MC1R* genotype (see below) improved this only slightly to 74%.[270] In another model, the strongest predictors of invasive CMM in adults aged 40–69 years were age, sex, tanning ability, number of naevi at age 21 years, and number of prior skin lesions treated destructively.[257]

A range of non-UV-related risk factors have been recently described. In a Danish study, the risk of CMM was increased in association with higher birth weight, and being tall in both childhood and adolescence, but not in relation to body mass index or body surface area.[227] The birth weight finding is consistent with some,[5, 254] although not all[223] previous studies; if a real finding it may indicate that an increased risk of CMM originates early in life, potentially driven by processes that regulate childhood height and/or birth weight. An inverse association between risk of CMM and a history of atopy (a genetic tendency to develop allergic diseases such as hay fever, asthma, and eczema) may reflect heightened immune surveillance in the skin of people with a history of atopic (allergic) dermatitis.[218]

Aetiology: genetic risk factors. High-risk genes for CMM include those involved in skin pigmentation, tumour suppressor pathways (e.g., the cyclin-dependent kinase inhibitor 2A *(CDKN2A)* found in 20% of familial CMM cases), immune suppression, and telomere maintenance.[276] The *MC1R* gene is well recognised as an important regulator of skin

pigmentation. The R (null) alleles of *MC1R* are strongly linked to red hair, freckling, and sun sensitivity, and to inefficient DNA repair and increased apoptosis (controlled cell death) of melanocytes. In white participants with a histopathologically confirmed CMM, the presence of an R allele was associated with a 42% (95% CI 15–76%) higher UV-signature mutation load compared to not having an R allele. This approximately equates to the higher mutation load associated with an additional 21 years of age.[292] New gene polymorphisms associated with increased susceptibility to CMM are being identified;[368] these may improve understanding of mechanistic pathways and provide potential opportunities for the development of novel therapeutic agents. Additional detail of recent research on the pathogenesis of CMM is provided in the supplementary material.

Incidence of CMM around the world. The incidence of CMM is highest in fair-skinned populations, particularly those living in locations with high ambient UV radiation, e.g., Australasia, but also some countries with low annual UV radiation, e.g., Norway, Denmark, and the Netherlands.[173] The incidence increases with increasing age.[56, 143] Globally, the increasing incidence of CMM from 2005 to 2015 (56%) was exceeded only by that of prostate (66%) and thyroid cancers (99%).[130]

Temporal trends in the incidence of CMM are variable by country or region (see **Table 1**). That is, while the age-standardised incidence rate (ASIR) continues to increase in some countries, it appears to have peaked in others, and the incidence in younger age groups is decreasing in several countries and/or regions; for example in the USA,[127] Australia,[74, 371] and New Zealand,[371] possibly as a result of strong sun protection programs beginning in the 1980s. In Denmark, the increases in incidence have been particularly steep in the elderly (70 years and older).[30]

Table 1 **Incidence of cutaneous malignant melanoma and changes over time in recently released data and publications**

Location[Reference]	Year	Age Standardised Incidence Rate (ASIR)* per 100,000		Change in incidence (average annual % change, AAPC)	
		Male	Female	Male	Female
*United Kingdom[56]	2000	13.7	14.3		
	2010	24.3	22.0	+7.7%	+5.4%
	2014	28.0	24.1	+3.8%	+2.4%
**USA (whites)[159]	2000	28.5	19.1		
	2010	36.2	24.8	+2.7%	+3.0%
	2014	38.8	26.1	+1.8%	+1.3%
^Canada[120]	1992	9.8	8.9		
	2010	17.2	14.5	+4.2%	+3.5%
*Denmark[30]	1989–2003	14.9	17.3		
	2004–2011	23.5	27.8	+5.2%	+5.5%
*Denmark[154]	1985–1987	7.3	8.7		
	2008–2012	21.6	24.7	+4.5%	+4.3%
*Iceland[334]	1990–1999	5.9	10.9		
	2000–2009	10.2	16.5	+7.3%	+5.1%

Location[Reference]	Year	Age Standardised Incidence Rate (ASIR)* per 100,000		Change in incidence (average annual % change, AAPC)	
		Male	Female	Male	Female
*Netherlands (thin melanoma, < 1 mm)[358]	1994–1997	4.9	8.8		
	2006–2010	9.1	15.0	5.0%	4.3%
***Estonia[263]	1995	~4.1	~5.5		
	2013	8.6	11.3	+4.4%	+3.8%
*South Tyrol, Italy[10]	1998–2002	12.2	13.3		
	2008–2012	23.1	23.1	+8.9%	+7.4%
*Catalonia, Spain[278]	2000	5.1	6.1		
	2007	6.3	6.5	+3.4%	+0.9%
***Australia[21]	2000	42.8	31.9		
	2010	45.3	30.9	+0.6%	−0.3%
	2014	46.1	32.5	+0.4%	+1.3%
***New Zealand[230]	2000	37.5	35.4		
	2013	39.4	35.8	+0.4%	+0.1%
*Israel[315]	2006	19.0			
	2010	16.0		−3.9%	
***Iran[282]	1996	0.48	0.42		
	2000	0.50	0.55	+1.0%	+7.7%
***Africa (total)[246]	2004	5.1	3.9		
	2013	4.9	2.9	−0.4%	−2.8%
***South Africa (whites only)[246]	2004	20.5	16.1		
	2013	19.7	13.8	−0.4%	−1.6%
***Costa Rica[79]	1985–1989	1.3	0.9		
	2003–2007	2.5	2.2	+5.1%	+8.0%

* European Standard Population; ** US Standard Population 2000; *** World Standard Population; ^ Crude incidence.
Note that the reference population for standardisation varies across studies, limiting comparability across studies.

Data from the USA, UK and Australia showed that the age-specific incidence of CMM increased over 17 sequential 5-year birth cohorts from 1895–1899 to 1975–1979, but the slope of the increase was decreasing.[86] These changes are likely to be due to both external factors that affect all age groups equally (e.g., changes in diagnostic criteria) and cohort effects that are specific to the unique experience of a particular age group as they move through time (e.g., preference for a tan, sun protection education in childhood).[86]

The importance of factors other than ambient UV radiation is exemplified by the rapid increase in CMM incidence in Estonia that began following that country's transition to an open market economy in the 1990s. This was possibly driven by increased use of tanning beds and holidays in sunny locations,[263] although part of the increase could have been due to earlier and more accurate detection of CMM. The importance of cultural differences (for example, clothing habits) and probably degree of skin pigmentation, was shown in a study

comparing the incidence of CMM in five Iranian provinces (1996–2000) with locations in the USA matched on levels of ambient UV radiation. Despite the similarity in ambient UV radiation, the age-standardised incidence rates were 38-fold higher for men and 36-fold higher for women in the USA compared to Iran.[238]

Changing patterns in CMM mortality. Melanoma was the cause of nearly 60,000 deaths globally in 2015.[173] Age-standardised mortality rates due to CMM have stabilised in some countries, probably due to a combination of prevention through sun protection programs, earlier detection, and improvements in treatment. For example, in the USA, the mortality rate of 2.7 per 100,000 persons in 2011 was the same as in 1982,[143] and in Australia, mortality was stable at around 6.0 per 100,000 from 2004 to 2012.[21] In light-skinned people globally, the peak birth years for CMM mortality were 1936–1940 in Oceania, 1937–1943 in North America, 1945–1953 in the UK and Ireland and 1957 in Central Europe. For people born later than these years in each location, the lifetime risk of death from CMM decreased and, for those born in 1990–1995, the risk level was similar to that of people born before 1900–1905.[23]

Incidence of CMM in people of different ethnicities. The incidence of CMM is lower in people with darker skin; for example, in the USA (2010–2014) it was 31.6 per 100,000 population in non-Hispanic whites *vs.* 4.7 in Hispanics and 1.1 in African Americans.[159] In addition, incidence is stable in Hispanics and African Americans but increasing in non-Hispanic whites. When CMM does occur in people with dark skin, it is typically found on the sole of the foot, under the fingernail (collectively referred to as acral lentiginous melanoma), or on other sites that are not highly sun-exposed. Medical care is often sought at an advanced stage with a consequent poorer prognosis.[215] Differences in incidence of CMM are not only due to protection arising from greater levels of melanin in the skin. Hispanics who adopt the behaviours and norms of a USA lifestyle (e.g., preference for a tan, not using sun protection), and Hispanics who are born in the USA, have a higher risk of sunburn and CMM compared to those who retain their traditional lifestyles.[115]

Keratinocyte cancers. The KCs are the most common cancers in many light-skinned (predominantly Caucasian) populations. Although they are less likely to be lethal than CMM or internal cancers, they incur high costs and can be a source of considerable disability due to disfigurement either from the cancer or the treatment.

Aetiology: environmental risk factors. The primary cause of KC is exposure to solar UV radiation. It has been estimated that essentially all KCs that occur in Australia are attributable to the high exposure to solar UV radiation, and that 10% of SCCs that would otherwise have occurred in 2010 were avoided due to regular sunscreen use.[259]

The patterns and timing of sun exposure (i.e., intermittent *vs* continuous; early life *vs* cumulative) in relation to the different types of KC, remain somewhat unclear. While SCC is clearly associated with cumulative exposure to the sun, the patterns that underpin risks of BCC are more complex. This is best exemplified by the body site distribution of the two cancer types. Whereas SCC occurs almost universally on body sites that are frequently exposed to the sun (i.e., face, head, forearms, hands, and lower legs), a significant proportion of BCCs occur on the trunk,[336] suggesting a role for intermittent sun exposure. This hypothesis is supported by the findings of a recent study among French women where recreational sun exposure was more strongly related to BCC, and total and residential sun exposure were more strongly related to SCC.[306] The use of sunscreen with a high sun protection factor (SPF) prior to the age of 25 was associated with reduced risk of BCC, but use after that age was associated with increased risk of both BCC and SCC, possibly due to higher sun exposure in sunscreen-

users during adulthood.[306] Similarly, in an Australian study, higher ambient UV radiation at the location of residence during early life (birth and up to 20 years) was associated with an increased risk of BCC but not SCC, and the risk of SCC but not BCC was associated with long-term cumulative sun exposure assessed by self-reported work outdoors.[185] BCC is the most common of the KCs, so this emphasises the need to focus on protection from sun exposure early in life.

Aetiology: phenotypic risk factors. Several phenotypic factors are associated with risk of KC, primarily because they influence the dose of UV radiation that reaches the target cells of the skin. A recent study from Australia found that self-reported skin colour, tanning tendency, and freckling all contributed significantly to predicting the risk of KC.[372]

Aetiology: genetic risk factors. Multiple genome-wide association studies (GWAS) (for example, refs [61, 331]) have identified germline genetic variants that alter risk of BCC. The BCC susceptibility loci identified in the most recent GWAS clustered into five functional categories: telomere biology, immune regulation, epidermal differentiation, non-coding RNA, and pigmentation.[61] These are mostly consistent with previous findings. An analysis of variants in vitamin D receptor binding sites identified several that were associated with BCC risk, supporting a potential role for vitamin D in BCC carcinogenesis.[202]

Most germline variants associated with SCC risk are pigmentation loci.[18, 59] GWAS have also identified other variants, including in genes involved in tumour interaction with the immune system, anti-apoptotic pathways, and cellular proliferation. Larger effect sizes are seen in younger age groups, highlighting the greater impact of environmental factors in SCCs that arise at older ages.

Several rare inherited genetic disorders influence the risk of KC and help to elucidate possible mechanisms underpinning their aetiology. For example, the genetic disorder, xeroderma pigmentosum (which also increases risk of CMM and see section 4.2.2), is caused by mutations in genes in the nucleotide excision repair pathway. The function of the gene products in this pathway is to repair UV-induced photoproducts. Mutation in these genes results in a very high frequency of KC at a young age; overall, the incidence is 150 times higher than in the general population, and in patients under 20 years the incidence is 5000 times higher.[183]

A possible role of HPV in the aetiology of SCC was identified by studying patients with epidermodysplasia verruciformis. These patients have increased susceptibility to infection with some HPV subtypes, resulting in widespread hyperproliferative lesions that develop into SCCs in up to 60% of patients.[212] The hypothesis that HPV may influence risk of SCC in people without epidermodysplasia verruciformis is not yet confirmed, but a new rodent model supports the view that HPV and UV radiation act synergistically to increase risk of SCC.[150] These findings provide impetus for further exploration of the interaction between UV radiation and HPV in the aetiology of cutaneous SCC in humans, and perhaps indicate that vaccination against some HPV subtypes may have a role to play in prevention of SCC in the future. More detailed information on the pathogenesis of KC and the role of HPV is given in the supplementary material.

Incidence around the world. In some locations, the incidence of KCs outnumbers that of the major internal cancers by a factor of 40.[274] BCC outnumbers SCC, although the ratio depends on age and sex; a study in Australia reported that, in women and men aged 40–44 years, the ratios were 12:1 and 8:1 respectively, but in people aged 65–74 years the ratio was approximately 2:1 in both sexes.[264] Similarly, in a USA northern Californian

population, the ratio of BCC to SCC in 31 to 45-year-olds was 5:1, but those aged over 60 years had approximately the same number of BCCs and SCCs.[60]

Although death from KC is uncommon, morbidity is significant, with a large economic impact (see section below). However, accurately measuring incidence rates and monitoring trends over time is difficult, because many lesions are treated destructively without prior biopsy, and KCs are generally not recorded in cancer registries because of the large numbers of both lesions and people affected.

The highest incidence of KC occurs in Australia. Individuals often present with multiple KCs, so it is important to consider both person-based and lesion-based incidence (with the latter always higher than the former). A recent report based on data from Australia's universal health insurance scheme (Medicare) estimated that the person-based incidence (2011–2014) for KC excisions was 1531 per 100,000 people per year. The ASIRs for BCC and SCC were estimated as 770 and 271 per 100,000 people per year, respectively.[264] Almost half (47%) of those treated during the study period had two or more KCs excised. Thus, the lesion-based incidence rate for excisions was 3154 per 100,000 people per year and, if destructive treatments were included, this increased to 4458 per 100,000 people per year. Recently reported incidence rates from other countries with Caucasian populations are considerably lower, as seen in **Table 2**.

Table 2 **Incidence of keratinocyte cancers worldwide**

Incidence*	Years	Incidence rate per 100,000 per annum		
		All keratinocyte cancer	SCC only	BCC only
**Australia[264] Person-based Lesion-based	2011–2014	 1531 3154	 271	 770
**Auckland (New Zealand)[274] Lesion-based	2008	 1906	 522	 1385
***North Rhine-Westphalia (Germany)[333]	2015	188 (Men) 149 (Women)		
^Nordic countries[98]	2011–2015	18 (Men) 12 (Women)		
***United Kingdom[98]	2002–2006	99	23	76
#Minnesota (United States)[243]	2000–2010		163	321
^Lesser Antilles[69]	2000–2010		15	
^South Korea[255]	2011–2014		1	2
¥South Africa (Black Africans)[251]	2000–2004		3 (Men) 2 (Women)	3 (Men) 2 (Women)

* Person-based incidence is reported unless otherwise specified; ** Age-standardised to the Australian (2001) population;
*** Age-standardised to the European standard population; ^ Age-standardised to the world standard population;
# Age-standardised to the United States (2010) population; ¥ Population used for age standardisation not reported.

Incidence of KC in people of different ethnicities. There are limited recent data on the incidence of KC from countries without predominantly Caucasian populations, but reported rates are at least an order of magnitude lower (**Table 2**).

Trends in KC incidence. In almost every location where trends have been monitored, there is evidence of a substantial increase in incidence of KC over time (see **Table 3**).

Table 3 **Trends in keratinocyte cancer incidence in recent publications**

Location (reference)	Years	Change in incidence (average annual % change, AAPC)					
		BCC		SCC		KC	
		Male	Female	Male	Female	Male	Female
South Korea[255]	1999–2014	+8.0%	+9.0%	+3.3%	+6.8%		
Spain (Girona)[297]	1004–2012	+1.0%	+2.0%		+1.6%		
Germany[195]							
Schleswig-Holstein	1999–2012					+2.3%	+3.3%
Saarland	1999–2012					+6.0%	+6.3%
Nordic countries[98]	2006–2015					+3.1%	+3.9%

Despite the increasing burden of KC around the world, there is evidence of a decrease in younger populations in some locations. In Australia, the excision rates for KC declined significantly in people younger than 45 years between 2000 and 2011 (**Fig. 3**), and a similar decrease was also observed for lesions treated using destructive methods, e.g. cryotherapy (freezing).[258] The incidence rate in younger groups also decreased in British Columbia in Canada[1] and was stable in northern California.[17]

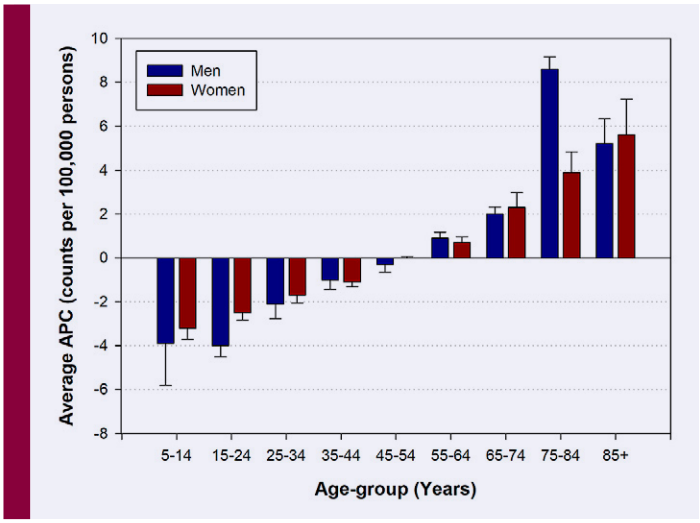

Fig. 3 **Average annual percentage change (AAPC) with 95% confidence interval of excision rates for keratinocyte cancer in Australia 2000–2011 by age-group (from ref.[258] reproduced with permission).**

Merkel cell carcinoma. Merkel cell carcinoma (MCC) is a rare, highly aggressive, skin cancer mainly affecting the elderly and the immunosuppressed; for example, there is an increased risk following solid organ transplantation. Tumours are typically solitary and found on sun-exposed areas of the skin. They are commonly located in the dermis, arising from epithelial stem cells or early stage B-lymphocytes, rather than the neuroendocrine Merkel cells as was originally thought.[305]

MCC can be 'virus-positive' or 'virus-negative' depending on the presence or absence of the Merkel cell polyomavirus. Exposure to UV radiation is thought to be important to disease pathogenesis in both virus-positive and virus-negative MCC.[33] In the northern hemisphere, most cases of MCC are virus positive (> 80%),[341] whereas in regions with high levels of ambient UV radiation virus-negative tumours predominate. Virus-negative tumours have a particularly high load of UV-signature mutations.[145]

The incidence of MCC is increasing in light-skinned populations but is highly variable across the world. The highest rates are in Australia and New Zealand, with the latter reporting an incidence of 17.6 per 100 000 between 2002 and 2011 in those aged > 85 years.[9] Incidence appears to be higher in men than women. MCCs typically metastasize early and have a poor prognosis.

Populations at particularly high-risk for UV-induced skin cancers. Immunosuppression following solid organ or stem cell transplantation greatly increases the risk of all forms of skin cancer, particularly SCC. The occurrence of these tumours on sun-exposed skin points to UV radiation acting synergistically with immune suppression.[134]

A recent review found standardised incidence ratios (SIR) (comparing the incidence in transplant recipients with that in the general population) for SCC in kidney transplant recipients ranging from 81 in Denmark to 121 in Sweden.[214] SIRs were even higher in people who had received heart transplants: 113 and 198 in Denmark and Sweden, respectively. However, risks are declining with newer, more individualised, immunosuppressive regimens and better advice about personal protection against sun exposure. A study in more than 8000 transplant recipients in Norway found that the SIR for SCC in those receiving transplants between 1983 and 1987 was 103; this had declined to 22 in people who received their transplant between 2003 and 2007.[289]

The incidence of CMM is also increased following organ transplantation (e.g., a two-fold increase following heart transplantation[313]), hematopoietic stem cell transplantation,[291, 356] and in other immunosuppressed states, e.g., HIV infection.[256]

Health costs of skin cancers. A recent economic analysis from Australia that included costs of diagnosis and treatment of CMM, as well as management of lesions subsequently found to be benign, estimated the cost of CMM to be *ca* AUD 272 million per year.[97] In the USA, the annual cost of treating newly diagnosed CMM is estimated to increase from USD 457 million in 2011 to USD 1.6 billion in 2030.[142]

The high incidence of KC poses a substantial economic burden. KC accounted for 8.1% of all health system spending on cancer (excluding screening) in Australia in 2008–2009.[22] The total cost of treatment in 2010 was *ca* AUD 512 million.[110] KC accounted for 5% of total cancer healthcare expenditure in the USA in 2007–2011 (total cost USD 4.8 billion).[142] Even in countries where the incidence is lower, the costs of healthcare are substantial. For example: Sweden (2011), *ca* 39 million EUR;[100] UK (2008), GBP 106–112 million (depending on the method used to calculate costs);[357] South Africa (2014–2015), USD 13.8 million.[135] A systematic review found that, relative to population size, the costs of treating KC were highest in Australia, with a cost to population ratio of 16 (2013 EUR per person), followed by New Zealand (ratio ~6), and Sweden (ratio ~4).[136]

A systematic review suggests that sun protection campaigns are cost-effective.[136] An analysis of the benefits of mass-media campaigns in New South Wales, Australia, found that for every dollar invested there was a return of AUD 3.85.[93] A modelling study for Australia found that for an additional investment in skin cancer prevention of AUD 0.16 per capita, 140,000 cases of skin cancer would be prevented from 2011 to 2030.[322]

Interaction with increasing ambient temperature. A study from 10 years ago suggested that higher temperatures may amplify the induction of human KC by UV radiation.[359] More recent results provide only limited support for such an effect.[111] The incidence of BCC increased in association with greater lifetime residential ambient UV radiation ($P < 0.0001$); there was also an increase in incidence with higher residential ambient temperature, but this was not statistically significant ($P = 0.09$). In analyses stratified by quintile of ambient UV radiation, the incidence of BCC increased with increasing ambient temperature, but this was statistically significant only in the third quintile of ambient erythemally weighted UV

radiation (P = 0.03; 184–196 J m^{-2}). The finding of a significant effect only in the third quintile (and not the 4th or 5th), suggests that this may be due to chance.

Interaction with air pollution. Particulate matter (PM) and polycyclic aromatic hydrocarbons (PAHs) cause skin carcinogenesis in animal models (reviewed in ref.[391]). The mechanism may be through the production of reactive oxygen species (ROS), generated mainly by UV-A wavelengths, and subsequent DNA damage.[51] There is little specific evidence in human studies, although the combination of sun exposure and cigarette smoking increases the risk of SCC and malignant lesions of the lip,[19, 179] most likely because of direct deposition of tar on the lips from the combustion of tobacco. Because the major route of exposure of humans to particulate air-pollutants is via the respiratory system (see Chapter 6), this interaction is unlikely in humans.

4.2.2 Photodermatoses

Photodermatoses are inflammatory skin disorders induced or exacerbated by exposure to UV radiation, and in some cases visible radiation.[247]

Pathogenesis. The photodermatoses fall into five groups based on their underlying aetiology; a brief overview and some examples are listed below.

(i) Dysregulated immune responses to UV and/or visible radiation. Examples include: polymorphic light eruption, which may be caused by a UV-induced reaction involving specific inflammatory proteins (interleukins, IL) of the IL-1 and/or IL-36 family;[196] chronic actinic dermatitis, which may be a delayed-type hypersensitivity reaction to UV radiation;[275] solar urticaria, which is a rapid onset, immune disorder mediated by mast cells, possibly due to photo-induced allergens that bind to immunoglobulin E.[45]

(ii) DNA repair disorders; for example, xeroderma pigmentosum (see section 4.2.1). Most patients with xeroderma pigmentosum have abnormal erythemal sensitivity to sunlight,[316] and a marked increase in risk of CMM and KC.[87]

(iii) Intrinsic biochemical defects (metabolic disorders), such as the rare disorders, erythropoietic protoporphyria[13] and X-linked protoporphyria, which are caused by mutations leading to defects in the synthesis pathway for haem, a component of the red pigment (haemoglobin) in red blood cells.[29, 216] Absorption of photons (maximal activation ~405 nm) by excess accumulated porphyrins (specific to the disease) results in the formation of reactive oxygen species (ROS) that can activate cutaneous pain sensors. This may be the origin of the severe skin pain experienced in erythropoietic protoporphyria.

(iv) Phototoxic and photoallergic reactions to drugs and exogenous chemicals. Many drugs and chemicals cause phototoxic and/or photoallergic reactions, triggered by the UV-absorbing properties of the agent or its metabolites.[389] Phototoxicity can occur through damage by ROS,[46, 281] or drug binding to DNA, as with psoralens (used with UV-A phototherapy to treat psoriasis).[68] Included is the systemic photosensitivity occurring with many medications (for example, anti-hypertensive drugs such as thiazides,[365] and non-steroidal anti-inflammatory

13 The porphyrias are a group of conditions in which chemicals (porphyrins) are abnormally increased in the body.

drugs),[175] and the photocontact reactions occurring with sunscreen filters, topical non-steroidal anti-inflammatory drugs,[101] and sap from some plants.[83] The photosensitivity is largely induced by UV-A but also UV-B radiation.[78] The factors that influence personal susceptibility to this photosensitivity are poorly understood.[175] Increasing evidence also suggests long-term exposure to certain photosensitising drugs, e.g., voriconazole, can increase the risk of CMM or KC.[72, 309]

(v) Photoaggravation of existing disorders. Photosensitivity occurs in a proportion of patients who have disorders with an underlying immune pathogenesis. For example, a high percentage of people with systemic and cutaneous lupus erythematosus are photosensitive,[186] and exposure to UV radiation can induce flare-ups of disease activity.[107] The skin disorders psoriasis and atopic dermatitis are most commonly ameliorated by exposure to UV radiation. However, a subset of patients with psoriasis have severely photosensitive psoriasis,[299] and approximately 5% of patients with atopic dermatitis develop photoaggravated atopic dermatitis. The reason for this switch from a UV-responsive to a UV-aggravated disorder is unclear.[96]

Incidence of photodermatoses. While large epidemiological studies are scarce, certain photodermatoses are highly prevalent. In a multicentre survey of 6995 indoor workers, polymorphic light eruption was found to affect approximately 18% of the European population.[286] Drug photosensitivity occurs in 4% of patients under investigation for photosensitivity.[78] Several conditions are rare diseases, including chronic actinic dermatitis and solar urticaria; the prevalence in Scotland, UK, is estimated at 16.5 and 3.9 per 100,000, respectively.[77]

Incidence in different skin types/ethnicities. Polymorphic light eruption is reportedly less common in India (0.6% of attendees at a skin outpatient clinic)[318] and China (0.7% of a population sample).[82] Examination of 631 primary patient visits to a HIV dermatology clinic found HIV-related photosensitivity in 7.3% of the African American patients (versus 5.4% of all patients).[39] While individual photodermatoses show differing prevalence and demographics, overall they remain common in people of darker skin.[319, 338]

Morbidity due to photodermatoses. Clinical features of photodermatoses depend on the disorder and include severe phototoxic pain, burning erythema and itching, blistering, eye involvement (including conjunctivitis and pterygium), and incapacitating systemic symptoms. Photodermatoses cause major negative impacts on patients;[169] both their clinical manifestations and the need for light avoidance have consequences for schooling, employment, family and social activities,[332] and mental health.[290]

Possible future effects of changes in UV radiation and climate on the photodermatoses. The photodermatoses are triggered by exposure to UV radiation, often with demonstrable UV dose-thresholds for their provocation. Many conditions show a seasonal pattern, with their expression most pronounced in, or even restricted to, the spring and summer months. Accordingly, the impact of polymorphic light eruption was shown to follow the variation in level of ambient UV radiation across seasons in several locations in Europe.[205] Changes in UV radiation as a result of recovery of stratospheric ozone depletion, and changes in exposure as a result of global climate change may consequently alter the incidence and severity of a range of photodermatoses, including drug-induced photosensitivity.

4.3 Adverse effects on the eye as a result of exposure to UV radiation

Exposure to sunlight is a known or suspected risk factor for several eye diseases that can cause moderate or severe visual impairment; for example, cataract and age-related macular degeneration (see section 4.2.2).[109] Despite the high disease burden, there is a lack of awareness about sun protection for the eyes. For example, in a cross-sectional study of university students in north China (n = 386), over 90% were aware of the effects of UV radiation on sunburn and skin cancer, but only 28% were aware of increased risk of cataract, and 3% of risk of pterygium. Protection of the eyes during sun exposure was uncommon.[113]

When sunlight impinges on a normal healthy eye, it passes through the cornea, the intraocular lens, and the vitreous humour to reach the retina (**Fig. 4**). Radiation with wavelengths < 300 nm is largely absorbed by the cornea. In young children (up until around 10 years of age), UV radiation of wavelength around 320 nm can be transmitted by the lens.[34] The wavelength of peak absorption by the lens increases with age, from around 365 nm at age 8 years, to ~400 nm in adulthood and ~450 nm at age 65 years, although there are considerable differences between individuals.[34] Thus, UV radiation may reach the retina in the child, but not in the healthy adult eye.[385]

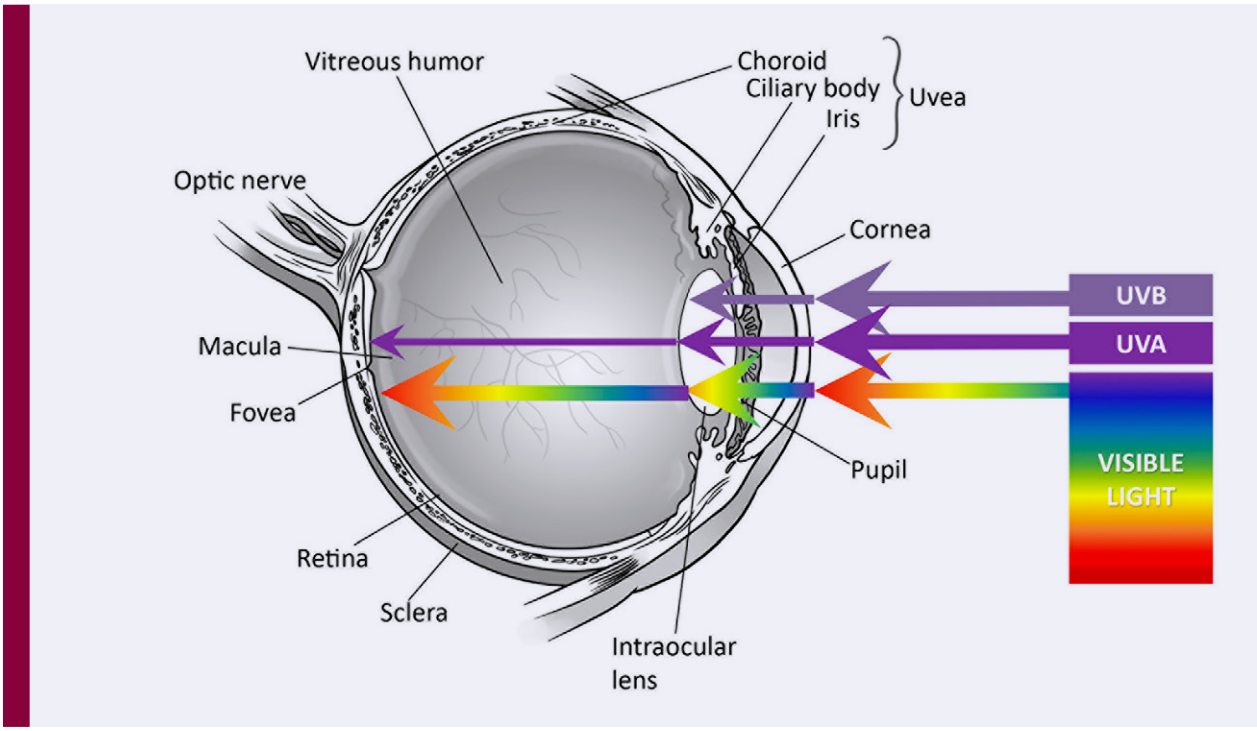

Fig. 4 **Schematic of the anatomy of the eye, showing the penetration of solar UV and visible radiation of different wavelengths in the healthy adult eye.**

4.3.1 Effects on the superficial layers of the eye

Exposure of the cornea or the conjunctiva to high-intensity UV radiation causes photokeratitis or photoconjunctivitis, respectively. Prolonged exposure of these superficial structures, such as through sun exposure over the lifetime, can result in pterygium,[345] pinguecula, ocular surface squamous neoplasia,[193] and, probably, melanoma of the conjunctiva.[288]

Pterygium. This is a wedge-shaped growth on the conjunctiva or cornea. It is not malignant (although it can contain pre-malignant cells) but if it extends over the cornea it can impair vision. Treatment is by surgery to remove the pterygium; however, this may not be universally available and often needs to be repeated for recurrences.

The prevalence of pterygium increases with age, and is often higher in men, those with outdoor occupations, and in populations living at high altitude. The highest prevalence is between latitudes 40°N and 40°S, an area known as the 'pterygium belt'.[70] For example, 39% of adults aged 20 years and over had a pterygium in Gondar (altitude 2133 m), northwest Ethiopia (within the pterygium belt), with the prevalence nearly four-fold higher in outdoor, compared to indoor, workers.[11] In a hospital-based study in Cambodia, the majority of the patients diagnosed with pterygium lived in rural areas (80.3%) and had always worked outdoors (61.2%).[67] A meta-analysis of risk factors for pterygium showed a linear reduction in the pooled prevalence of pterygium with increasing latitude band.[206] The incidence of pterygium decreased from 3.0 to 1.3 per 1000 person-years between 2004 and 2013 in South Korea, possibly due to improved awareness of the importance of eye protection and a reduction in outdoor occupations, such as farming, fishing, and forestry, over time.[287]

Heat, dust, and low humidity are thought to also contribute to the genesis of pterygium. In a study from Pakistan, 87% of people with pterygium lived in hot dry conditions.[317] In a large study from western Rajasthan, India (n = 5012), people with a pterygium had a three-fold greater risk of also having spheroidal degeneration of the cornea, for which the risk factors are thought to be low humidity, strong winds, and small injuries from sand particles.[232]

Pinguecula. Commonly associated with UV radiation and ageing, pinguecula is characterised by the development of benign, yellowish, slightly raised, nodules on the nasal side of the conjunctiva, in a similar location to pterygia. These lesions are most often asymptomatic but can be unsightly, become inflamed, or cause dry eye syndrome. Pinguecula can be very common. For example, in a population-based study in rural eastern China (126°E 31°N), pinguecula was identified in 76% of the population aged ≥ 50 years. Older age and outdoor occupation were strongly associated with higher prevalence of pinguecula.[192]

Ocular surface squamous neoplasia. Ocular surface squamous neoplasia (OSSN) refers to malignant lesions on the cornea and conjunctiva that may occur over a pinguecula or be apparent within excised pterygia.[314] Chronic exposure to UV-B radiation (especially in people with lighter skin type), HIV/AIDS, and infection with HPV are major risk factors for the development of OSSN. The incidence of OSSN is relatively high in African countries because it is more common for multiple risk factors to co-occur.[285] For example, ASIRs of 3.4 and 3.0 cases per 100,000 population per year were found for men and women respectively, in Zimbabwe[124]) compared to the USA (< 1 per 100,000).[231]

Exposure to UV radiation may initiate the development of OSSN through some combination of DNA damage, local and systemic immunosuppression, and reactivation of latent HPV infection.[123] In a study from Kenya, greater time spent in sunlight, less use of hats, having

more outdoor occupations, and lower education were associated with higher prevalence of OSSN.[122]

Conjunctival melanoma. Melanomas of the eye are rare, and conjunctival melanoma accounts for only *ca* 5% of these.[164] In Denmark, the annual incidence rates of conjunctival melanoma increased from 0.36 per million per year in 1960–1969 to 0.87 per million per year from 2000–2009,189 in parallel with rising incidence of CMM (see **Table 1**), supporting exposure to UV radiation as a common risk factor. Findings of a strong UV-mutational signature in tumour samples[288] lends further weight to a role for exposure to UV radiation.

4.3.2 Effects on the deeper structures of the eye

Absorption of UV radiation by the lens, and penetration beyond the lens, depends on the wavelength (**Fig. 4**), and varies according to age and the transparency of the lens.

Cataract of the lens. Cataract occurs when the lens, a small transparent disc-shaped tissue in the eye, develops cloudy patches. Over time, these patches increase in size and number, and cause blurry vision and blindness. Cataract is the leading cause of blindness worldwide (12.6 million people blind and 52.6 million people with vision impairment due to cataract in 2015).[109] Due to the wide accessibility of replacement surgery of the opaque natural lens with an artificial one, cataract-related vision loss is uncommon in developed countries. However, poor access to effective surgery as a consequence of lower socioeconomic status and/or lack of proximity to appropriate medical facilities can result in cataract-associated loss of vision in both developed and developing countries.[241]

Long-term exposure to UV radiation is a major cause of cataract, particularly those of the cortex and, perhaps, those located at the back of the lens, just under the capsule of the lens (posterior sub-capsular).[222] These cataract types commonly make up over 50% of all cataracts, although this varies with age and location. A high prevalence of cataract, especially cortical[339] and posterior sub-capsular, with a younger age of onset, was found to be a major contributor to age-related visual disability in a high altitude (higher UV-B radiation), compared to a low altitude, region of China.[122] Another study estimated that an increase in the daily ambient erythemal UV radiation of 1,000 J m^{-2} was associated with the cataract-related loss of an additional 92 disability-adjusted life years (DALYs) per 100,000 population.[394] The burden of disease (in DALYs per 100,000) was much higher in the elderly (< 65 years old: 34; 65–74 years: 607; ≥ 75 years old: 1,342) and in an agricultural population compared to a non-agricultural population (177 *vs* 81).[394]

Age-related macular degeneration. In adults, longer wavelength UV-A, visible, and infrared radiation reach the retina and may cause degeneration of retinal tissue.[129] UV-B radiation can reach the retina in young children. Higher exposure of the eye to solar radiation is thus a plausible risk factor for age-related macular degeneration (AMD), a leading cause of blindness worldwide.[267]

AMD develops when that part of the eye responsible for central vision (the macula) loses function. The underlying mechanisms of AMD are not yet clear, but probably include oxidative stress, mitochondrial dysfunction, and inflammation.[320] There are two main types of AMD. Dry AMD occurs when the macula is damaged by the build-up of lipid deposits. This is the least severe, but most common form of AMD (90% of all cases), and results in gradual

loss of central vision occurring over many years. Dry AMD may progress to the more severe wet, also called neovascular, AMD. Here, there is leakage from abnormal blood vessels that have grown from the choroid into the macula, or there is a build-up of fluid/blood exerting a physical force on the macula. If untreated, central vision deteriorates within days or weeks.[199] Clinically, AMD is often defined as early, intermediate or late stage, based on the size and the number of lipid deposits under the retina. The disease burden of AMD is increasing; globally the age-standardised loss of DALYs due to AMD increased from 5.3 to 6.3 per 100,000 between 1990 and 2016,[117] with vision impairment due to AMD affecting 8.4 million people.[109]

The association between stage of AMD and exposure to the sun remains unclear. In a case-control study of 3701 Europeans, past sunlight exposure (≥ 8 hours outside daily) was associated with increased risk of early (odds ratio (OR) 5.54, 95% CI 1.25, 24.58) and late (OR 2.77, 95% CI 1.25, 6.16) AMD after adjustment for age, sex and smoking behaviour.[307] Working outdoors was associated with late (OR 2.57, 95% CI 1.89, 3.48) but not early (OR 1.20, 95% CI 0.85, 1.71) AMD in the same study.[307] However, in a study in Bordeaux, France (n = 963 residents aged 73 years and over), both low and high lifetime ambient UV radiation (compared to intermediate) were associated with increased risk of early, but not late, AMD.[81] It is not clear what the biological pathways could be to support this apparent U-shaped association. The inconsistency in the findings across various studies may relate, at least in part, to the challenges of accurately measuring sun exposure to the eye over a lifetime, and failure to account for possible confounding factors. Nevertheless, these indications of a link with sun exposure, for a disease as serious as AMD, support public health measures recommending that the eye be protected from excessive exposure to solar radiation.

Uveal melanoma. Uveal melanoma (UM) involves the iris, ciliary body, or choroid (collectively known as the uvea). It is rare (incidence of 5.1 cases per million per year in the USA from 1973–2008[326]) but has high mortality; only 69% of patients will survive beyond 5 years.[184] There is little direct evidence of an association between UM and exposure to UV radiation, but people with markers of a sun-sensitive phenotype are at increased risk. For more information, see supplementary material.

Pseudoexfoliation syndrome and glaucoma. Pseudoexfoliation syndrome (PXF) is an uncommon age-related disorder characterised by accumulation of protein in the drainage system of the eye. It can cause glaucoma, the second most frequent cause of blindness.[262] Recent evidence suggests that the risk of PXF increases with greater time outdoors and a history of work over water or snow, and is reduced with the use of sunglasses.[268] However, the evidence is not consistent. Long-term protracted sun exposure (≥ 5 hours/day) was associated with a non-significant 3-fold increase in risk of PXF (OR 2.76, 95% CI 0.96, 7.96), P = 0.06) based on 16 cases (prevalence 0.12%), in a population-based study in South Korea;[177] however, there was no evidence of an association in older residents (≥ 50 years) of an isolated island in Korea.[194]

4.3.3 Future predictions taking account of changing UV radiation and interactions with climate change

There are not yet any quantitative projections of UV-induced eye diseases that consider the effects of global climate change. Based on our knowledge of risk factors, reduction in snow and ice cover because of global warming, as well as lower UV radiation at high northern latitudes in the future, should result in a reduction in the risk of UV-induced eye diseases,

because of the reduced dose from both direct, and more importantly, reflected radiation. On the other hand, drought and wildfires, with loss of vegetation, will result in increased reflected and diffuse UV radiation (particularly important for exposure of the eye), and release of particulate matter into the troposphere. This is a 'perfect storm' for pterygium – low humidity, high heat, high dose of UV radiation, dust and other particulate matter. The risks will not be evenly spread; in high latitude (typically high-income countries), risk will be decreased and good access to surgery for cataract and pterygium reduces the risk of visual impairment. Rural, poor, and populations in drought areas, may have reduced access to surgery, and thus suffer the dual burdens of visual impairment and loss of livelihoods.

4.4 Other health risks linked to exposure to solar radiation

We have previously reported[26] on emerging evidence of links between greater exposure to UV radiation and an increased risk of several other disorders, including goitre and thyroid cancer,[226] Parkinson's disease,[64, 75] and mania.[225] The supporting evidence remains sparse.

In France, the incidence of B-cell acute lymphoblastic leukaemia in children aged less than five years was higher with higher levels of erythemal UV radiation at the location of residence, above a threshold of 100 J m^{-2} (daily average UV radiation dose over the period 1988–2007).[71] Further studies are required to substantiate this association.

5 Beneficial effects on human health from exposure to UV radiation

The best-known beneficial effect of exposure to UV radiation is the cutaneous synthesis of vitamin D. Immune suppression due to exposure to UV radiation, occurring through vitamin D and non-vitamin D pathways, has both benefits and adverse effects on health.[207] The adverse effects of UV-induced immune suppression are described above; evidence for benefits is considered below, along with benefits of exposure to UV radiation for vision and other health outcomes.

The commonly accepted marker of vitamin D status is the concentration of 25-hydroxyvitamin D (25(OH)D) in serum or plasma. Exposure to solar UV radiation within the preceding 1–2 months is a major determinant of 25(OH)D concentration.[178] Thus, while the concentration of 25(OH)D in serum or plasma is the accepted marker of vitamin D status, it is also an estimate of recent exposure to solar UV radiation. "Sufficient" recent sun exposure could be construed as that which results in "sufficient" 25(OH)D (see below). Randomised placebo-controlled trials of vitamin D supplementation test the health benefits of vitamin D alone, separately from UV-induced production of vitamin D that may have benefits unrelated to vitamin D, as discussed below.

5.1 Vitamin D

Vitamin D is produced in the skin following exposure to UV-B radiation. There are a small number of substantive food sources, such as oily fish and certain types of mushrooms, and vitamin D is also available as a supplement. Irrespective of the source, vitamin D is hydroxylated in the liver to 25(OH)D and in the kidney to the active form, 1,25-dihydroxyvitamin

D ($1,25(OH)_2D$). The active form of vitamin D can also be produced from 25(OH)D by a wide range of cell types that have the requisite enzyme, allowing autocrine (effects on the cell producing the $1,25(OH)_2D$), paracrine (effects on nearby cells), as well as endocrine (effects on distant cells through changes in blood levels) signalling.[174]

There is a lack of consensus on the criteria (in terms of concentration of 25(OH)D) that define the categories of vitamin D status – deficiency, insufficiency, sufficiency. In 2011, after a comprehensive systematic review of the literature, the National Academy of Medicine (USA) concluded that a concentration of 25(OH)D in serum or plasma of 50 nmol L^{-1} is sufficient to optimise the bone health of most people.[162] The 2016 report of the Scientific Advisory Committee on Nutrition (SACN) in the UK recommended that the serum 25(OH)D concentration should not fall below 25 nmol L^{-1} at any time of the year.[311] A recent study showed that a 25(OH)D concentration of ~30 nmol L^{-1} was sufficient to optimise bone mineral density and a range of markers of muscle strength and function in middle-aged women.[380] Possible mechanisms of action of active $1,25(OH)_2D$ for multiple health outcomes are described briefly in the supplementary material.

5.1.1 Prevalence of vitamin D deficiency

The lack of consensus over the definition of deficiency, combined with historic challenges in measuring the concentration of 25(OH)D, make it difficult to document the international prevalence of vitamin D deficiency and any temporal trends. However, there are now standardised measurement protocols and rigorous quality assurance schemes resulting in more comparable measurements across studies and over time. The importance of this is highlighted in a study from Germany in which the results of three national health surveys conducted from 1998 to 2011 were retrospectively standardised. In all studies, the mean 25(OH)D after standardisation was higher than in the original study.[279]

Studies using standardised methods indicate that low vitamin D status is common in many parts of the world. For example, across a range of northern European countries the annual mean prevalence of 25(OH)D concentration of < 50 nmol L^{-1} was found to be 40%, with 13% having a 25(OH)D concentration of < 30 nmol L^{-1}.[57] Dark-skinned ethnic subgroups were much more likely to have 25(OH)D levels < 30 nmol L^{-1} than light-skinned groups (three times higher in the UK and 71 times higher in a Finnish immigrant population).

A high prevalence of vitamin D deficiency in northern Europe is not surprising, since modelling shows that that there is not enough ambient UV-B radiation to produce sufficient vitamin D for at least 4 months over winter in Germany, Ireland, the UK, Denmark, Finland, and Iceland.[253] In light of this, the UK SACN recently recommended routine supplementation of 400 IU per day to maintain 25(OH)D levels > 25nmol L^{-1}.[311] Fortification of food may also be an effective way of mitigating the risk of vitamin D deficiency. In Finland, for example, fortifying liquid milk products resulted in a decrease in the prevalence of severe deficiency (25(OH)D < 30 nmol L^{-1}) among people not using supplements from 13% to less than 1%.[165]

In the USA, National Health and Nutritional Examination Surveys (NHANES) found no change in the mean 25(OH)D concentration (after assay standardisation) from 1988 to 2006 (~62 nmol L^{-1}), but an increase of 5 nmol L^{-1} from 2007 to 2010, partly due to supplementation. The prevalence of a vitamin D insufficiency < 50 nmol L^{-1} was ~30% from 1988 to 2006 and 26% in 2009–2010. Less than 7% of the study population had a 25(OH)D concentration of < 30 nmol L^{-1}.[308] Data from the Australian National Health Survey show that *ca* 23% of the population had low vitamin D status (< 50 nmol L^{-1}), with 6% < 30 nmol L^{-1}.[20]

There are limited data on the prevalence of vitamin D deficiency in low- and middle-income countries. A recent systematic review found that two-thirds of low- and middle-income countries had virtually no data that could be used to determine the prevalence of vitamin D deficiency.[58] Among the 29 countries with data available, at least 20% of the population, or of an at-risk population subgroup (infants, children, women of child-bearing age, pregnant women), were vitamin D deficient (< 25 to 30 nmol L^{-1}) in five countries (Afghanistan, Pakistan, India, Tunisia and Mongolia). This suggests a public health issue warranting mitigation.

5.1.2 Vitamin D and health

The role of vitamin D in health remains controversial, apart from the established association between vitamin D and musculoskeletal health. Low concentrations of 25(OH)D have been linked to increased risk of a broad range of health conditions. However, it is not clear whether the low 25(OH)D level causes the health condition or is an effect of it (called reverse causation). In addition, issues in the study design or analysis of the data (e.g., selection or measurement bias, or uncontrolled confounding factors) may account for the associations described.

Vitamin D plays a critical role in calcium homeostasis and vitamin D supplementation is widely recommended in older people to avoid osteoporotic fractures. A recent meta-analysis of cohort or nested case-control studies found that low serum 25(OH)D concentration (defined as < 50 nmol L^{-1} in most included studies) was associated with significantly increased risk of total fractures and hip fractures,[106] but the results did not enable a criterion for 'sufficiency' to be derived. Meta-analyses of randomised trials of the effect of vitamin D supplementation on bone mineral density[284] or fracture[392] do not suggest that supplementation is of benefit in community-dwelling (i.e., not institutionalised) adults. This conclusion is supported by Mendelian randomisation studies[14] (see footnote for explanation), which found no association between genetically determined 25(OH)D concentration and bone mineral density, bone metabolism markers, or fracture.[198, 348]

A recent review of meta-analyses and randomised controlled trials concluded that there is limited evidence that supplementation with vitamin D has any effect on health other than musculoskeletal conditions.[344] However, two meta-analyses, one using individual patient data, found evidence that vitamin D supplementation caused a modest reduction in upper respiratory tract infections,[220, 367] mainly confined to those who had low vitamin D status.[42] A Cochrane review[15] and meta-analysis found some evidence that supplementation can reduce all-cause and cancer mortality in middle-aged and older people, but could not exclude that the results may be due to chance.[40]

Despite observational studies suggesting inverse associations between concentration of 25(OH)D and risk of cardiovascular disease, supplementation trials have failed to find effects on endothelial function,[161] arterial stiffness,[293, 354] or hypertension.[37] Mendelian randomisation studies are inconclusive, with one of the two published studies finding that higher genetically-determined 25(OH)D concentration was associated with reduced systolic and diastolic blood pressure and reduced odds of hypertension,[364] but the other finding no association.[187]

14 Mendelian randomisation is a method used to control for reverse causation and confounding factors. It uses genetic polymorphisms known to affect 25(OH)D concentration as an instrumental variable to test, in large populations, a causal association with a disease outcome.

15 Cochrane reviews are systematic reviews of primary research in human health care and health policy; they are recognised internationally as the highest standard in evidence-based health care.

There is considerable and consistent support for an association between higher concentration of 25(OH)D and reduced risk of the autoimmune disease, multiple sclerosis (MS),[327] including from a Mendelian randomisation study.[234] Indeed, vitamin D deficiency is commonly considered an established risk factor for the disease.[16] Lower 25(OH)D concentration at birth[250] and during adulthood[242] may both be important. However vitamin D supplementation trials in people with MS have thus far failed to demonstrate a clinical benefit.[323]

Observational studies consistently show associations between low 25(OH)D concentration and increased risk of colorectal cancer.[95] However, to date, trials have found no benefit of vitamin D supplementation, and two Mendelian randomisation studies suggest there is no causal link between 25(OH)D concentration and colorectal or other cancers.[88, 343]

The role of vitamin D in maternal or foetal outcomes during pregnancy is controversial. Observational studies show a link between low concentrations of maternal 25(OH)D and increased risk of pre-term birth,[393] but a high quality meta-analysis found no beneficial effect of vitamin D supplementation.[295] Two meta-analyses found that vitamin D supplementation during pregnancy was associated with reduced risk of being small-for-gestational age,[38, 295] but a study published since then found that supplementing pregnant women in Bangladesh, where vitamin D deficiency is common, had no effect on infant length-for-age scores at 1 year of age.[296]

5.2 Beneficial effects on immune function

Defence against microbial attack of the skin rests on the integrity of the surface, the innate immune response, and the adaptive immune response. UV irradiation damages the skin surface but upregulates innate immune responses while also modulating (largely suppressing) adaptive immune responses (see section 3.2). UV-induced local suppression of cellular immunity may have benefits for skin disorders such as psoriasis and atopic dermatitis, while systemic suppression may be beneficial for disorders such as for autoimmune disease and allergy. These are discussed in the sections below.

Recent publications focus on the balance, following exposure to UV radiation and upregulation of vitamin D synthesis, of immune suppression and upregulation, and innate *vs* adaptive immunity, for effects on the skin microbiome,[269] the development of childhood food allergy,[335] and the seasonality and outcomes of infectious diseases.[2] Much work remains to be done to understand these effects, including the impact of the exposure dose and the time course of exposure, on the direction and magnitude of any effects.

5.2.1 Beneficial effects of UV radiation on immune-related skin disorders

The beneficial effects of exposure to UV radiation in skin disorders are wide ranging, including enhanced skin barrier function, reduced epidermal cell turnover, epidermal and dermal cell apoptosis, in addition to many further anti-inflammatory effects, and the modulation of innate and adaptive immune responses.[149] Exposure to UV radiation, as used therapeutically in phototherapy, ameliorates a number of immune-mediated skin diseases, including psoriasis, atopic dermatitis, polymorphic light eruption, and vitiligo.[24] Suppression of psoriasis can be prolonged, which may be attributable to restoration of T_{reg} cell numbers.[112] A discussion of the mechanisms of phototherapy and effects in these disorders is included in the supplementary material.

5.2.2 Systemic suppression of adaptive immunity

Several studies have reported an association between higher levels of sun exposure or ambient UV radiation and reduction in (autoimmune) inflammatory bowel disease: risk of Crohn's disease (hazard ratio (HR) = 0.49, (95% CI 0.23, 1.01) for the third *vs.* the first tertile of ambient UV radiation, (*P* for trend = 0.04),[167] paediatric Crohn's disease (increase in incidence of 0.23 per 100,000 population for each 10° increase in latitude),[158] and hospitalisation (reduction of 0.44 cases per increment of UV radiation in MJ m^{-2} per day (95% CI –0.82, –0.05, P = 0.03),[166] and need for bowel surgery for both ulcerative colitis and Crohn's disease (Crohn's disease: relative risk (RR) = 1.24, (95% CI 1.16, 1.32); Ulcerative colitis: RR = 1.21, 95% (CI 1.09, 1.33), for low UV index (0–2) compared to high UV index (≥ 8).[200] However, findings from cross-sectional and case-control studies of lower 25(OH)D levels in people with IBD than those who do not have the disease[13] may be due to reverse causality. There is some support from animal models that exposure to UV radiation is important in reducing risk or activity in inflammatory bowel disease through both vitamin D and non-vitamin D pathways.[43]

Low concentrations of 25(OH)D in early childhood were associated with an increased risk of wheeze in one study (*P* < 0.005 for adjusted OR of wheeze at 10 years of age in association with number of follow-up visits where the child had low 25(OH)D levels)[156] and, in a meta-analysis, low maternal 25(OH)D levels were associated with an increased risk of persistent asthma in the offspring (pooled OR = 0.84, 95% CI 0.70, 1.01, *P* = 0.06, comparing the highest with the lowest category reported in each study).[105] Whether these effects are causal, vitamin D- or non-vitamin D-mediated, is not yet clear.

Higher levels of sun exposure over the lifetime are associated with reduced risk of developing MS (for example, adjusted OR = 0.70, 95% CI 0.53, 0.94) for each increment in lifetime UV dose increment of 1000 KJ m^{-2})[207, 210, 349, 360] through plausible biological pathways.[207] Further support for these findings comes from a recent multi-ethnic case-control study in the USA, where higher levels of lifetime exposure to UV radiation were associated with reduced risk of early MS consistently across whites, Hispanics, and African-Americans (adjusted OR = 0.53, 95% CI 0.31, 0.83, *P* = 0.007 in African Americans; adjusted OR = 0.68, 95% CI 0.48, 0.94, *P* = 0.02, in whites; adjusted OR = 0.66, 95% CI 0.42, 1.04, *P* = 0.07).[188] This is in contrast to the increased risk in association with low levels of 25(OH)D, which was apparent only in whites.

The lack of effect of supplementation with vitamin D on clinical relapse in people with MS has been noted above. There is, however, some evidence of benefit from UV radiation. For example, there is a well-described seasonal variation in disease relapses in people with MS, and this demonstrates latitudinal variation, with a shorter gap between relapses in people living at higher latitude (lower levels of UV radiation).[330] In a longitudinal cohort study, conversion to MS (in people who had had a first, isolated, demyelinating event (FDE), the most common precursor of MS) and relapse activity were lower in those with higher lifetime sun exposure (with no association with 25(OH)D concentration at initial participation in the study following the FDE).[324] Furthermore, participants who increased their sun exposure after a FDE had a significantly reduced risk of conversion to MS and subsequent relapse. Finally, a recent clinical trial showed that people with an FDE who were randomised to receive an 8-week course of phototherapy had a 30% lower risk of developing MS within 12 months.[147] However, the results were not statistically significant, probably because of the small sample size (n = 10 in phototherapy and control groups).

Admissions to hospital for anaphylaxis (a severe allergic reaction) increased with increasing latitude (> 34° S) and lower levels of ambient solar UV radiation in children in Chile.[160] This

is consistent with a previously described latitudinal gradient in anaphylaxis described in Australia.[240]

5.3 Benefits for eye health and vision

There is accumulating evidence that lack of sun exposure in childhood increases the risk of myopia (short-sightedness). Myopia occurs when the eye is too long, or the lens or cornea focus light too strongly; incoming light thus focuses in front of the retina (rather than on the retina) resulting in blurry vision. Although myopia can be corrected with spectacles, contact lenses and/or surgery, severe myopia, may lead to blinding eye diseases (cataract, glaucoma, retinal detachment, and myopic maculopathy) in later life.[73]

The prevalence of myopia is increasing rapidly in many countries. Around 80% of 20-year-olds in many East and Southeast Asian countries[91] and 38% of young adults (aged 18–24 years) in the USA are myopic.[366] Intense study during school years and less time spent outdoors are two major factors thought to account for this rapid increase.[236]

In an elderly European population (mean age 72 years), an increase of one standard deviation in exposure to UV-B radiation (determined using self-reported sun exposure and meteorological data) during teenage years and in early adulthood was associated with a 20–30% reduction in risk of being myopic.[375] In two large trials in China, interventions to increase time outdoors during and after school hours in schoolchildren reduced the incidence of myopia by 9% over a 3-year intervention in 6-year-olds, and by *ca* 5% in a one-year intervention in 6–11-year-olds.[151, 168] However, it remains unclear what element of 'time outdoors,' i.e., whether it is the strength of the irradiance outdoors or the need to focus on objects at a variety of distances, that provides this protective effect.

The evidence for a role of vitamin D deficiency in risk of myopia is mixed, with some studies showing an association,[65, 346, 384] but no evidence of effect in others, including using the Mendelian randomisation approach.[73, 141, 375] The contrasting findings could reflect differences in study designs, reverse causality (whereby individuals with myopia spend less time outdoors), or that the 25(OH)D level is simply a proxy for time outdoors, with some other element of 'time outdoors' the causal factor. For example, exposure to UV radiation or the higher intensity of shorter wavelength (blue) visible light encountered outdoors compared to indoors, may protect against the development of myopia by slowing elongation of the eyeball.[283, 347]

5.4 Additional health benefits

High blood pressure is the risk factor responsible for the second greatest loss of DALYs globally (89.9 million in 2016).[118] Observational studies and a single intervention study support a possible benefit of sun exposure for high blood pressure, potentially through UV-A-mediated release of nitric oxide stores in the skin that cause arterial vasodilation and reduction in blood pressure.[370] Furthermore, exposure to UV-B radiation may inhibit the development and progression of atherosclerosis through modulation of inflammation.[303]

In a prospective study in southern Sweden, adults with high intentional sun exposure had a lower risk of cardiovascular disease (CVD), and death due to a cause unrelated to cancer or CVD, than those who avoided sun exposure.[203] Avoidance of high-dose sun exposure was a risk factor for death of similar magnitude to smoking in this study.[203] Several studies also support this association of low sun exposure with higher rates of all-cause mortality, mainly

increased risk of death from CVD and other non-cancer diseases (reviewed in[204]). Whether these associations are vitamin D-related, attributable to exposure to UV radiation per se, or working through other pathways, such as exercise, is unclear.

Higher sun exposure is associated with reduced risk of some cancers, but it is difficult to determine whether this is causal. Lower incidence of colon cancer in Finnish fishermen and women could be due to higher exposure to UV radiation (reflected in the higher incidence of lip cancer in this population), or presumed higher consumption of fish.[352] It is particularly hard to interpret ecological studies showing lower incidence of cancers (for example, non-Hodgkin lymphoma[54] and multiple myeloma[233]) at lower latitude or where there is higher UV-B irradiance, as it is difficult to adequately adjust for possible confounding factors.

6 Risk *vs* benefit of exposure to solar and/or UV radiation

The balance between risk and benefit of sun exposure depends on the size of the effect, the proportion that can be attributed to high or low exposure, and the total health burden of the outcome. There is convincing evidence (reviewed above) that exposure to UV radiation is a risk factor for a number of adverse health effects; the proportion of those diseases that is attributable to exposure to UV radiation has been quantified.[259] However, there is not yet conclusive evidence that low sun exposure causes disease, or, if it does, the size of the disease burden incurred.

We have previously reported on the balance between DNA damage and synthesis of vitamin D.[26] Short-term, high-dose sun exposure increased levels of 25(OH)D, at the expense of accompanying DNA damage (assessed using a urinary biomarker).[272] In contrast, low-dose regular irradiation with solar-simulated UV radiation (3 times weekly for 6 weeks) increased 25(OH)D concentration while producing DNA damage (CPDs on skin biopsy) that was partially repaired at 24 hours post-exposure.[104] Importantly, the damage did not accumulate over the course of UV irradiation indicating adequate repair between exposures. Both the pattern and the dose of exposure appear to be important, as is the time post-exposure that the damage to DNA is measured. A study in children on holiday by the Baltic Sea showed that exposure to UV radiation that resulted in borderline erythema was accompanied by a 25% increase in concentration of 25(OH)D, but also a large increase in DNA damage (assessed using a urinary biomarker 24 hours after the last exposure to the sun).[245]

A recent study assessed the balance of increasing 25(OH)D levels *vs* whole epidermal CPDs in people across the full range of skin types (I–VI) for different sub-erythemal doses (20%, 40%, 60% and 80% of their personal minimum erythemal dose (MED)) of solar-simulated UV radiation.[321] Levels of both whole-epidermis CPDs and serum 25(OH)D increased according to the MED dose fraction (i.e., UV dose adjusted for skin type); even the lowest dose of UV radiation (0.2 MED) resulted in a gain in 25(OH)D but also induced CPDs, across all skin types. There was, however, a marked difference across different skin types in the CPDs in the basal cells where the carcinogenic risk is highest: from undetectable in dark skin types (IV–VI) even at the highest MED dose, to significantly increased in light skin types (I–III) even at the lowest MED dose.[321] Thus, skin type is important in framing sun protection messages: lighter skin is very sensitive to DNA damage,[103] but vitamin D production is similar across skin type groups for similar MED dose fractions of UV radiation. Notably, at 48 hours post-irradiation,

there had been DNA repair and there was no difference in CPD levels in skin between exposed and unexposed controls, for any skin type.

For high-burden diseases, such as hypertension,[370] possible beneficial effects of sun exposure that only minimally increase adverse effects (e.g., skin cancer) may greatly alter the balance of risks and benefits of sun exposure.

Future projections for ambient UV radiation[25] are that UV-B radiation will be lower in 2075–2095 compared to 1955–1975 at high latitudes, with particularly marked reductions in the winter months. UV-B radiation is likely to be higher in the tropics, and over cities that are currently heavily polluted, with regulation of air pollution leading to clearer skies. These future projections have important implications for the balance of risk and benefits of exposure to UV radiation. That is, in high northern hemisphere locations where low vitamin D status is already common, there may be an increased risk of vitamin D deficiency, although this may be offset by warmer temperatures that encourage people to spend more time outdoors with more skin exposed. In the tropics, the risks of adverse effects may be increased, particularly if these populations also adopt Western preferences for tanning and sunny holidays.

7 Protection from the health risks of sun exposure

The health risks of sun exposure can be mitigated through appropriate sun protection behaviours, but the degree of protection required depends on individual susceptibility to damage from exposure to UV radiation. The photoprotection needs, and the balance of risks and benefits, of people with dark skin differ from those with light skin.[103, 321]

Weather forecasts and several apps for mobile phones provide information on the UVI to guide whether sun protection is required. Recommendations are that, when the UVI is 3 or higher, protection should be used.[379] Protection of the skin and eyes involves a suite of options, best used in combination. Staying out of the sun, and wearing clothing, hats, and sunglasses are of primary importance. Sunscreen is typically a second line of defence, particularly useful for body surfaces that cannot be covered by clothing, such as the face and hands. Nevertheless, sunscreen was the most frequently nominated sun protection strategy in a large sample (n = 4217) of people living in Western Australia, particularly amongst adolescents and women.[180]

7.1 Hats and clothing

Hats protect the scalp and provide shade to different parts of the face, depending on the hat type and the elevation of the sun. A wide-brimmed hat offers the best cover, with a typical protection factor of 5 to the nose and ears, and 2–3 to the cheeks, while baseball caps provide good protection to the nose but leave ears, cheeks and neck unprotected. Legionnaire style hats have a flap of fabric covering the neck and ears, making them particularly effective at protecting these sites.[84]

Clothing provides good photoprotection, depending on the weave, colour and fabric type (e.g., natural or synthetic). The UV protection factor (UPF) for fabric is comparable to the sunscreen protection factor (SPF) used for sunscreen. Shirts with a loose weave, such as linen, have a lower UPF (ranging from 5 for white to 15 for black materials), whereas tightly woven cotton t-shirts have a UPF of ≥ 40.[4] However, clothes with a high UPF fabric may have limited coverage. Thus, a garment protection factor (GPF) has been proposed as a new metric that takes account

not only of the UPF of the fabric but also the body surface area covered.[94] There are three nominal categories of sun protection: 0 to < 3 (minimal), 3 to < 6 (good), and ≥ 6 (excellent).

7.2 Sunglasses

Recommendations for sun protection typically include the use of UV-certified sunglasses (for example, Sun Smart Australia,[55] and the World Health Organization[379]).

Both spectacles and contact lenses provide partial eye protection from UV radiation. Regular plastic spectacle lenses achieve higher protection against UV radiation than glass lenses; however, both need to have a UV-protection coating for full safety.[294] Other lens materials including polycarbonate, most high refractive-index plastics, and photochromic lenses inherently block 100% of UV radiation without a special coating. Commercially available soft contact lenses block *ca* 90% of UV radiation and limit the light reaching the cornea.[280] In a recent study, the use of contact lenses and spectacles was associated with a reduction in UV-induced damage (as measured by conjunctival autofluorescence) on the nasal side but not the outer side of the eye.[378] This was unexpected, as the UV-induced eye disorders (see section 4.3.1) are typically more pronounced on the nasal side.

Sunglasses provide excellent protection from UV radiation provided they have a wrap-around style; however, a large proportion of sunglasses purchased from unauthorised dealers in developing countries and distributed to developed countries do not conform with international standards for protection from UV radiation.[31] Often, the same sunglasses are kept and used for many years, although both the protection from UV radiation and the impact resistance of lenses deteriorates over time. New research suggests the current standard stress test (for ageing of sunglasses) is not adequate to assure safe use for two years (the average time a person keeps a pair of sunglasses) by users who wear them for a maximum of 2 hours a day.[221] A more appropriate test protocol has been proposed (including exposure to a solar-simulator for 67.7 hours at a distance of 50 mm from the lamp bulb). However, there is concern that the temperature rise in this experimental setup may adversely affect the optical properties of the lens.[221]

7.3 Shade structures

Shade provides broad-spectrum photoprotection and its provision is especially important in school playgrounds[89] and other play areas; it should be an architectural/landscaping consideration at the design stage of new buildings and/or parks, where it can provide photoprotection at no cost to the user. The efficacy of shade can be graded by its protection factor (PF), which is the ratio of the biologically effective UV (UVBE) irradiance on a horizontal plane in full sun to the UVBE under the shade structure.[265] The PF should be at least 15 for effective shade, although PFs of 30 or 35 are recommended.[265] The PF takes account of both the UPF, which is a measure of the attenuation of erythemal UV radiation by the material providing the shade, as well as the coverage in terms of both sky-view and UV radiation reflected from surrounding material.[265] Optimal shade includes having ground structures with low albedo (e.g., grass rather than concrete), cloth canopies with a UPF ≥ 20, and protection from both diffuse and direct UV radiation. A recent study showed that a beach umbrella alone does not provide sufficient protection for extended time in the sun.[261] Shade from trees or artificial structures reduces the direct incident UV radiation, but may not be effective in limiting exposure from indirect, e.g., reflected UV, depending on the angle of the sun and the surrounding surfaces.[312]

People may use shade to keep out of the heat, and thus serendipitously improve their sun protection. A recent trial of shade provision in parks in Denver (USA) and Melbourne (Australia) showed that people were more likely to use passive recreation areas (i.e., areas used for activities, such as sitting or standing while socialising, or watching sports) if shade structures were provided.[50] The authors concluded that public investment in shade provision was warranted for reducing the risk of skin cancer.

7.4 Sunscreens

Sunscreens are formulations of chemicals that are applied to the skin to attenuate solar UV radiation. Their active ingredients absorb and may scatter UV photons. The index of sun protection is the sun protection factor (SPF), which is the MED with sunscreen divided by the MED without sunscreen. SPF is primarily a measure of protection from UV-B radiation. It is determined under stringent prescribed laboratory conditions, including application of sunscreen at 2 mg cm^{-2} to human skin and exposure to solar-simulated UV radiation. While the determination of SPF is largely harmonised internationally,[386] UV-A protection and the labelling of sun protection products can vary according to the regulatory domain (e.g., EU *vs* USA). There remains considerable inter-laboratory variability in testing SPF, with coefficients of variation that exceed 50% in some cases,[229] although the new international standard for *in vivo* testing (ISO 24444) should improve standardisation.[163] In addition, new *in vitro* methods for SPF measurement are being developed.[228]

Reduction in the dose of UV-B radiation delivered to the skin due to sunscreen application in theory reduces vitamin D synthesis but, in practice, this may not be important because vitamin D synthesis occurs at sub-erythemal doses;[321] methods of sunscreen application are also imperfect (**Fig. 5**).

The MED of a fair-skinned person is 2–3 standard erythemal doses (SEDs; 1 SED = 100 J m^{-1} of erythemally weighted UV radiation).[146] Under idealised conditions, exposure of the skin to 45 SED through a sunscreen of SPF 15 transmits three SEDs to skin cells. This reduction in dose can be expected to reduce the risk of sunburn, as well as mutagenic DNA photodamage.[170, 260, 387] However, although sunscreens are UV-protective, it is not yet confirmed that the degree of protection against sunburn (i.e., SPF) equates to that against DNA photodamage (i.e., DNA-PF).

Fig. 5 **Left shows UV image with no sunscreen. Right shows image with SPF 50 sunscreen coverage in black. Note lack of application in the region around the eyes (photograph from ref.[277]).**

Regular use of sunscreen is associated with fewer naevi, a marker of CMM risk, in children.[235] A randomised controlled trial has shown that daily sunscreen use reduced the risk of SCC and CMM, but not BCC,[138, 139] although limitations of the study suggest that the conclusions should be viewed with caution.[301] Two other studies[121, 369] have reported that regular use of sunscreen was associated with reduced risk of CMM, i.e., regular use of sunscreen with SPF ≥ 15 was associated with an

18% reduction in the risk of CMM in women aged 40–75 years,[121] and greater use of sunscreen in childhood was associated with a 40% reduction in CMM before age 40 years.[369]

Dark skin pigmentation has been thought to provide a DNA-PF of ~6 compared with light skin. However, a recent comparison of white (phototype I/II) and black skin (phototype VI) shows DNA-PFs of 59.0 (95% CI 24–110), 16.5 (95% CI 11–27), and 5.5 (95% CI 4.5–5.5) for the basal, middle and upper epidermis, respectively.[103] The high DNA-PFs for the lower layers of the epidermis are more consistent with observed differences in incidence of CMM (*ca* 30-fold higher in white *vs* black Americans, see section 4.2.1) than the overall DNA-PF. The high DNA-PF for the basal layer of the epidermis suggests that in black populations, sunscreen is not required.

A "typical" woman (body surface area 1.6 m^2) on a beach holiday needs ~100 g of sunscreen per day for three whole body applications under SPF test conditions, and a 'typical' man (body surface area 1.9 m^2) needs 114 g. The "teaspoon rule" is a good rule of thumb guide for sunscreen application at 2 mg cm^{-2}.[310] This advises just over half a teaspoonful for each arm, and head and neck area, and just over a teaspoonful for each leg, anterior and posterior torso. Numerous studies have shown that people apply much less and therefore do not achieve the labelled SPF.[271] In surveys of people on a beach in Denmark, the percentage of women reporting having used sunscreen on a given day increased from 45% in 1997 to 78% in 2016; in men it rose from 39% to 49%.[152] Although the estimated quantity of sunscreen applied increased from 0.48 mg cm^{-2} in 1992 to 0.57 mg cm^{-2} in 2016, it remained too low for adequate protection.[152]

Poor application of sunscreen can also mean that some areas are not protected at all, including the eyelid and periorbital regions (Fig 5[277]); sunglasses may be a better option for this area.

A laboratory study showed a linear relationship between time spent on sunscreen application and the thickness of the sunscreen.[153] Furthermore, when participants applied sunscreen a second time, twenty minutes after the end of the first application, the mean thickness increased from 0.71 to 1.27 mg cm^{-2}. Thus, encouraging people to spend more time on sunscreen application and/or applying sunscreen twice, may result in better photoprotection.

A field study compared the effectiveness in preventing sunburn of sunscreens with SPFs of 50+ (application 1.1 ± 1.3 mg cm^{-2}) and 100+ (application 1.0 ± 0.98 mg cm^{-2}), using a randomised double-blind split-face design (n = 199) in natural sunlight at a ski resort.[374] Mean time outdoors was 6.1 ± 1.3 hours. Over half (55.3%) of the participants had more sunburn on the 50+ side and only 5% had more sunburn on the 100+ side, showing that even amongst high SPF sunscreens, there is better protection from 100+ compared to 50+.

7.4.1 Risks and potential risks of sunscreen use

Contact and photocontact allergy can occur with use of sunscreen products, the latter involving the absorption of UV radiation by a sunscreen filter; both conditions manifest clinically as acute dermatitis. Multi-centre studies show that contact and photocontact allergy may be more common than previously thought. For example, in a European study, 9.2% of 1031 patients with exposed-site dermatitis had photocontact allergy, and ~ 4% had contact allergy, to organic sunscreens.[101] The prevalence of contact allergy to a sunscreen agent was similar in a UK study (5.5%), but there was a lower prevalence of photocontact allergy (4.4%).[49] Identification of the culprit agent enables its avoidance, with selection of a different sunscreen required for photoprotection.

Exposure of the skin to UV radiation results in natural adaptation, through tanning and epidermal hyperplasia.[80] It is plausible that use of sunscreen nullifies this natural adaptation, potentially increasing the risks of the adverse effects of UV radiation when the skin is unprotected.[201] However, sunscreen use is safer than topical skin bleaching agents for those who favour a lighter skin complexion.[76]

In a study of 100 Latina teenagers in rural California, self-reported use of sunscreen was associated with 58% higher urinary concentration of the UV-filter, benzophenone-3.35 This filter has also been detected in human milk and urine.[155] However, no health effects in humans have so far been described.

Increasing concerns about the environmental risks of sunscreens (described in Chapter 4) has triggered interest in alternative molecules, such as mycosporine-like amino acids (MAA) that act as a 'sunscreen' in marine organisms.[66, 190] These have not yet been tested in humans.

7.5 Interventions to reduce harmful exposure to UV radiation

There is good evidence that multi-component, community-wide interventions can be effective in improving sun-protective behaviours, particularly sunscreen use, amongst children and adults.[302] These interventions use a combination of integrated strategies including mass media campaigns, environmental interventions (such as installation of shade structures) and policy changes implemented across multiple settings within the community. Interventions targeted to specific settings, including child-care centres, schools, outdoor recreational and tourism settings, and outdoor workers, can be effective in reducing the overall exposure to UV radiation of those who engage with these settings.

In Australia there has been a long history of multicomponent community-wide interventions,[325] supported by policies such as not applying sales tax to sunscreens with a high SPF and legislation requiring employers to protect their employees from the harms associated with outdoor work. The falling skin cancer rates in younger cohorts in Australia[371] are likely to be at least partially attributable to these population-wide intervention efforts. Similar trends have not been seen in the USA[371] and the UK[56] where intervention efforts have been sporadic[191] and generally underfunded to achieve the desired population-wide effect.[99]

7.5.1 Sun protection behaviour

There is continuing evidence of risky behaviour with regard to sun exposure in light-skinned populations.[209] Even where there are strong programs for protection against sun exposure, sunburn on at least one occasion in the previous year is common (e.g., 37% of adults in the 2010 USA National Health Interview Survey[157]), particularly in young adults (18–29 years, 52%), and those with light skin type (44%). Deliberate sun exposure also remains common (e.g., 78% of respondents in a telephone interview in France[304]). Australian adolescents desire a tan despite being aware of the long-term health risks.[340] In Hungary, 74% of 12–19-year olds had experienced at least one episode of serious sunburn, 5% purposely sunbathed daily, and 10% did not use any form of sun protection.[119] In Ireland, with the highest incidence of CMM in Europe, nearly 50% of a sample of Cork university students reported deliberate tanning in the previous summer.[108] Thus, despite health promotion programs to increase knowledge about the risks associated with sun exposure, risky behaviour continues.

A personal or family history of CMM does not reduce risky behaviour with respect to the sun, despite evidence that ongoing exposure of CMMs to UV radiation may promote metastasis.[28] A systematic review showed that a substantial proportion of people diagnosed with CMM reported subsequent sunbathing (up to two-thirds at least once since diagnosis), sunburns (60% at least once in a 3-year period) and indoor tanning (up to a quarter of survivors), and many did not practice skin self-examination.[244] Similarly, children of people who have survived CMM had higher sun exposure and sunburn than average-risk populations in a study from California.[128]

Exposure to the sun in childhood may be particularly important to risk of CMM and BCC in later life in light-skinned populations. In Australia, a 2011–2012 national survey found that 77% of primary schools had a written sun protection policy, and 75% of those without one were planning to develop one in the next 12 months.[92] Nevertheless, in a study from tropical north Queensland, Australia, fewer than 50% of schools had policies that shade should be provided during outdoor events, and even fewer that events should be scheduled to avoid the peak sunlight hours.[351] In a nationally representative sample of schools in the USA, sun safety practices and policies were uncommon.[102] For example, only 12% of high schools, 18% of middle schools and 15% of elementary schools scheduled outdoors activities to avoid times when the sun was at peak intensity.[92, 351] The trends of decreasing incidence of skin cancers in younger age groups[258, 371] could be reversed unless sun protection programs targeting exposure in childhood, adolescence, and in high-risk groups are continued.

7.5.2 The UV Index – is it still fit for purpose?

The UVI provides a measure of the erythemally weighted UV irradiance at the Earth's surface. It can be measured or calculated, and is often provided as a UV forecast, in the form of a whole number that is the maximum UV irradiance expected for the day. Current messaging for sun protection uses five categories of exposure: "low" (1, 2), "moderate" (3, 4, 5), "high" (6, 7), "very high" (8, 9, 10), and "extreme" (11 or higher); sun protection is recommended when the UVI is ≥ 3. For the biological effects of UV radiation, the dose (rather than the irradiance) is important; that is, consideration needs to be taken of both the UVI and the duration of exposure.[224] A recent study has shown that sunburn can occur at a UVI < 3 if there is sufficient duration of exposure,[224] and thus sun protection may be required even at low UVI. It has been recommended that messages about sun protection that use the UVI should be locally appropriate, e.g., extending the graphical representation to higher values in locations where the UVI reaches very high levels, or changing category criteria where the population is predominantly dark skinned.[126] A counter-argument is that messaging regarding sun protection should be globally consistent to enhance understanding and uptake. The UVI remains a useful tool for public communication on requirements for sun protection,[126] although there may be a need to provide more nuanced messaging incorporating duration of time in the sun.

7.5.3 New developments for sun protection

New tools are becoming available for monitoring personal sun exposure, such as electronic dosimeters and smartphone apps. These are reviewed in Chapter 1.

8 Future effects: changing stratospheric ozone, ambient UV radiation, and climate change

Predicted reductions in ambient UV radiation by 2100 as a result of recovery of the stratospheric ozone layer, and changes in cloud cover,[25] particularly at high latitudes, together with climate-induced changes in sun exposure behaviour,[383] will change the balance of risks and benefits for human health in any location. In addition to direct effects, through the pathways described above, these pressures will have a range of indirect effects. Food security will be affected as a result of alterations in terrestrial[44] and aquatic[376] ecosystems, as well as air pollutants such as tropospheric ozone.[377] This will be an important determinant of human health, both directly and as a driver of conflict, and climate change-induced migration. The interactive effects of climate change and UV radiation are changing the growing seasons of plants (see Chapter 3), including extending the duration of allergen production.[395] This has knock-on effects for human allergic disorders, increasing the risks and duration of hay fever and asthma. The interactive effects on ecosystem services such as disinfection of surface waters, including following extreme weather events, are discussed in Chapter 4. The potential impacts of changing stratospheric ozone (through changing ambient UV radiation) on the health effects that have been linked to climate change, and the potential impacts of climate change on the health effects of exposure to UV radiation, are summarised in **Table 4**.

Several of the occupations associated with renewable energy technologies are amongst the most rapidly growing in the USA,[353] but also incur a high risk of increased exposure to UV radiation, such as work associated with installation and repair of wind turbines and solar panels. Outdoor workers, such as farmers, may be particularly at risk from the combination of high levels of UV radiation and an increasing number of hot days.[144] Changes in behaviour, such as not working outdoors through the middle of the day, may be required.

UV radiation may adversely affect the physiology and insecticide tolerance of mosquitoes and this effect may be accentuated by environmental pollution.[342] The tiger mosquito *(Aedes albopictus)* is a vector for dengue fever. The female mosquito lays eggs in water-holding containers (for example, discarded tyres). A recent study showed that UV-B irradiation at levels to mimic full sun caused reduced survival compared to shade or no-sun conditions.[363] The importance of sun exposure and UV-B radiation received, in conjunction with global climate change, for the spread and geographic range of dengue and other mosquito-borne diseases is not clear.

Table 4. **Summary of potential health effects of changing levels of stratospheric ozone (via changes in ambient UV radiation) and of climate change, and possible interactions. Red arrows show potential effects of climate change on UV-related health outcomes; purple arrows show potential effects of UV radiation on climate-change induced health risks.**

Health-related effects of stratospheric ozone depletion through changes in UV radiation		Impacts of climate change and associated factors on UV-induced health effects
Skin cancers and photodermatoses: risk is increased with increased exposure to UV radiation	←	Warmer temperatures lead to increased time outdoors in cool locations, and less time outdoors where it is already hot. Warmer temperatures and air pollution may promote skin carcinogenesis

Health-related effects of stratospheric ozone depletion through changes in UV radiation		Impacts of climate change and associated factors on UV-induced health effects
Eye conditions: the risk of a range of acute and chronic eye diseases is increased with higher levels of UV radiation, but also other factors, such as particulates	←	Hotter, dryer conditions may increase the risk of pterygium; dehydration events (because of hotter, drier conditions) may increase the risk of cataract. Loss of snow and ice cover may reduce some eye disorders
Immunosuppression, including reducing risk of autoimmune conditions, such as multiple sclerosis	←	Warmer ambient temperatures worsen the symptoms of multiple sclerosis
Synthesis of vitamin D in skin and other potential benefits of UV irradiation of skin and eyes	←	Warmer ambient temperatures may change behaviour (as above) to increase or decrease time outdoors and covering clothing; warmer temperatures may increase the rate of chemical reactions in the skin, e.g., production of vitamin D. Higher precipitation may reduce time outdoors at high latitudes where vitamin D production is already marginal. Urbanisation, urban heat islands, urban "canyons" may reduce exposure to UV radiation
Health protection – sunscreens, hats, covering clothing, umbrellas	←	Warmer temperatures may make it less comfortable to wear hats, sunscreens and covering clothing, but make shade preferable

Impacts of changes in UV radiation on health risks of climate change		Health effects of climate change and associated factors
UV radiation is potentially insecticidal; lower levels because of recovery of the ozone layer may enhance climate change effects to increase risks of infection	→	Changing range of vector-borne, e.g., malaria and water-borne, diseases
Use of sun protection, e.g., clothing, hats, sunscreen, may exacerbate effects of increasing heat leading to greater risk of heat stroke	→	Increase in risk of heat stroke and heat stress because of increase in hotter days, warmer ambient temperature, and extreme heat events
UV radiation has an important role as a disinfectant of surface waters. Lower UV radiation because of recovery of the stratospheric ozone (and clouds) may reduce this effect, and increase the health risks following extreme weather events	→	Increased injury, death, contamination of freshwater supplies, because of an increase in extreme weather events
UV radiation has an important role as a disinfectant of surface waters	→	Increased risk of water-borne infectious diseases due to reduced availability of clean drinking water

Impacts of changes in UV radiation on health risks of climate change		Health effects of climate change and associated factors
Changes in food quality and quantity due to changes in UV radiation will positively or inversely interact with climate change effects	→	Challenges to food security (conflict)
Predicted reduction in UV radiation at higher latitudes will increase the risks of vitamin D deficiency and the loss of benefits of higher sun exposure, e.g., for blood pressure, autoimmune diseases	→	Climate change-induced migration of dark-skinned migrants, often from lower to higher latitude regions

9 Knowledge gaps

Our assessment of the recent evidence has highlighted several knowledge gaps that limit our understanding and assessment of the risks and benefits of exposure to UV radiation, and use of sun protection.

9.1 Vitamin D

Production of vitamin D occurs rapidly following UV irradiation of the skin; exposure to even low doses of solar-simulated UV radiation e.g., 0.2 MED, increases 25(OH)D levels[321] (this dose is achievable for a light-skinned person (skin type II) in ~10 mins at a UVI of 3). If the pre-vitamin D action spectrum is as suggested by recent work (reviewed in ref.[25]), exposure to UV-A radiation may cause a net loss of vitamin D synthesised in skin.[361] At low UVIs, it is possible to achieve considerable exposure to UV-A wavelengths, with potential adverse effects on health.[208] This raises further questions about the appropriateness of current messages that no sun protection is required when the UVI is less than 3.[224] Further work to better define the pre-vitamin D action spectrum is required. Considerable uncertainty remains about the health effects of vitamin D beyond musculoskeletal health and the mechanistic pathways, including the possible risks of over-enthusiastic, population-wide use of vitamin D supplements.[197]

9.2 Photodermatoses

More information is required of the possible risks to human health from exposure to higher levels of UV radiation with respect to the photodermatoses, including immune-mediated conditions, drug photosensitivity, and photoaggravated conditions. It is important that due attention is paid to this area in view of their high prevalence and morbidity.

9.3 Possible skin cancer risks associated with chemical bleaching of skin

Skin lightening or bleaching of melanin by mercurials, corticosteroids, and other compounds, often in unregulated formulations, is a global problem because it is associated with side effects such as dyschromia of skin, diabetes, and hypertension.[76, 300] Loss of melanin is likely

to lead to loss of photoprotection as noted in a report of cases of SCC in Senegal associated with cosmetic skin lightening.[213] There is a need for further research into the photobiological consequences of depigmentation, including in vitiligo.

9.4 Risks *vs* benefits of sun exposure

It remains impossible to make even qualitative assessments of the balance of risks and benefits, for populations or individuals, for several reasons. First, the totality of possible benefits is unclear, although mechanistic pathways are being elucidated. Second, there is little quantification of benefits for typical, 'real-life', patterns and amounts of sun exposure. Third, there is a range of complicating factors, such as skin type, genetics, and cultural habits for clothing and sun exposure, which make the balance highly variable, and therefore challenging to assess.

9.5 Uncertainties in sun protection

There has been a global trend, driven by consumer demand and industry marketing, to have higher protection from UV-A radiation in sunscreens, at the expense of UV-B protection for a given SPF. It is not established if this has an overall benefit or not. We need better understanding of the action spectra for the beneficial and adverse effects of UV radiation and their interactions. Better understanding is also required of the relationship between a sunscreen's SPF, i.e., the protection from erythema, and its DNA protection factor (DNA-PF), i.e., its ability to prevent DNA photodamage. While it is assumed that one provides a good measure of the other, this has not been confirmed experimentally.

There is recent interest in whether the action spectrum for erythema extends into the visible radiation wavelength range.[85] These wavelengths are not included in the laboratory assessment of SPF (which uses solar-simulated UV radiation); the actual SPF under natural conditions is not clear. Moreover, wavelengths from UV-B to UV-A and visible radiation can provoke photodermatoses, yet sunscreen protection factors for these conditions are not established.

While there has been a considerable increase in smartphone apps and devices for monitoring UV radiation, the impact on behaviour with respect to sun exposure has not been well assessed. This includes perseverance with the use of such devices, as well as long-term effects on behaviour.

9.6 Climate change-related unknowns

The size of the health effects of interactions between climate change and ozone depletion and recovery, e.g., for food security, allergy, climate change-induced migration leading to changes in the skin type distribution (and thus the balance of risks and benefits) of populations, and disinfection of surface waters by solar UV radiation, remains unclear. It is important to appreciate the full range of potential effects on human health, as input to imperatives to act on climate change. However, quantifying these effects is very challenging.

9.7 Interactive effects of exposure to UV radiation and air pollution

UV radiation initiates the chemical processes that lead to the production of photochemical smog (see Chapter 6). On the other hand, heavy air pollution blocks UV radiation from reaching the Earth's surface. Perhaps the most striking of the future predictions for levels of ambient UV radiation at the Earth's surface are for large increases over currently heavily polluted areas,[25] as that pollution becomes reduced by regulation and advances in technology.

9.8 Health risks of UV-related breakdown of environmental pollutants

UV radiation is a major source of breakdown of waste material (e.g., plastics and microplastics[12]) and chemical pollutants (e.g., pesticides and pharmaceuticals[337]) in the environment. The possible risks to health from the degradation products in the environment that may accumulate up the food chain is not yet clear.

10 Conclusions

Projections of ambient UV radiation under the combined effects of recovery of stratospheric ozone, current and future climate change, and climate change-induced changes in cloud cover, suggest lower levels in most regions not currently affected by high levels of air pollution (depending on the assumptions included in the climate change models used). Because of depletion of stratospheric ozone, there has been a strong focus on understanding the health risks of exposure to excessive UV radiation. There now needs to be improved understanding of possible benefits of having some exposure to UV radiation, and how this will be affected by the recovery of stratospheric ozone, in conjunction with the effects of climate change. In a predicted future of lower levels of UV radiation, lack of sun exposure may increase health risks, i.e., no longer receiving current benefits. At the same time, and for some years to come, we will continue to see the consequences of high past sun exposure, such as high skin cancer incidence, due to the lag between exposure and the occurrence of adverse effects.

Projections also show marked increases in UV radiation in specific regions because of clearer skies, e.g., over China. Increasing ambient UV radiation could be accompanied by higher incidence of skin cancer if there are accompanying changes in behaviour with respect to sun exposure, e.g., cultural changes toward sun-seeking behaviour because of adoption of more 'western' habits.

The Montreal Protocol stimulated intense research into the health risks of higher levels of UV-B radiation at the Earth's surface, particularly skin cancer. This has greatly improved our understanding of the disease burden and mechanistic pathways, leading in turn to better diagnosis and treatment. Additional research is now required to better understand the disease burden, mechanistic pathways, and personal susceptibility factors, for other adverse effects of exposure to UV radiation (e.g., the photodermatoses) as well as the broad range of potential beneficial effects.

In the future, there will be many interactions with factors related to stratospheric ozone and to global climate change – chemically in the stratosphere, but also through changing levels of ambient UV radiation and tropospheric air quality. The consequences of global climate

change will affect whole populations, for example, through forced migration because of rising sea levels, in ways that alter usual exposures to UV radiation. At the individual level, climate change may alter behaviours to receive more, or less, UV radiation, depending on acclimatisation to warmer temperatures. At this stage, we can only qualitatively note that such changes may occur and speculate on the possible or likely risks to human health.

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Supplementary material

This document contains additional detail in support of UNEP EEAP Report, Chapter 2; Human health in relation to exposure to solar ultraviolet radiation under changing stratospheric ozone and climate

1 Mechanisms underpinning changes in immune function following UV irradiation

1.1 Stimulation of innate immunity in the skin

Foreign microorganisms, as well as microbes that are part of the skin microbiome that have been damaged by UV radiation,[77] express pathogen-associated molecular patterns (PAMPs) that are recognised by the Toll-like receptors (TLRs) present on the membranes of keratinocytes and other cells of the innate immune system. Binding of the TLR with its specific ligand activates transcription factors that drive the release of pro-inflammatory cytokines (signalling molecules regulating immunity), chemokines (molecules inducing directed chemotaxis), and anti-microbial peptides (AMPs; for a review of AMPs, see[6]). Notably, the active form of vitamin D ($1,25(OH)_2D$) can be synthesised in the skin and induces synthesis of AMPs. These can be directly cytotoxic to pathogens and/or facilitate the cytotoxicity of natural killer cells and other cells of the innate immune system.[77]

In the skin there is considerable interplay between the innate and adaptive immune responses that may determine the nature of the immune response generated.[58] For example, AMPs can activate adaptive immune responses in the skin, and dendritic cells have properties of innate immune cells, but also present antigen to generate T-cell-mediated (adaptive) immune responses.[58]

1.2 Suppression of adaptive immunity

Exposure of the skin and eyes to UV radiation modulates adaptive immune function through pathways that are both vitamin D-dependent and independent of vitamin D (reviewed in[38], and shown in Fig. 1, main document). UV photons are absorbed by chromophores in the skin, including DNA, RNA, trans-urocanic acid (UCA), and membrane lipids, including 7-dehydrocholesterol, the precursor of vitamin D. The resulting products, including a range of cytokines and chemokines,[81] stimulate migration of epidermal (Langerhans cells, LC) and dermal dendritic cells to local lymph nodes. Interactions between LC and immune cells in the germinal centres of the lymph nodes lead to an upregulation of regulatory T (T_{reg}) and B (B_{reg}) cells, and dampening of cell-mediated immune processes.[38] Mast cell numbers are increased following UV irradiation;[36] release of tryptase by mast cells catalyses the conversion of pro-opiomelanocortin into a range of neuropeptides, including α-melanocyte stimulating hormone[102] that drives the tanning response.

Alterations in the skin microbiome following exposure to UV radiation[77] may also contribute to UV-induced immune suppression, and exposure to UV-B radiation alters the expression of immune-related genes,[14, 80, 81] possibly through epigenetic pathways. It is likely that there is considerable cross-communication between the different pathways that influence immune function.[81]

2 Cutaneous malignant melanoma

2.1 Pathogenesis of cutaneous malignant melanoma

The pathogenesis of cutaneous malignant melanoma (CMM), referred to as melanomagenesis, is a multi-step process, driven by mutations that alter cell growth, proliferation, differentiation, and cell death. CMM in younger people, and CMM occurring on the trunk, are more commonly associated with mutations in the *BRAF* gene (that encodes a key protein involved in control of cell growth).[59] In contrast, CMM in older people (associated with chronic sun exposure) more frequently demonstrate mutations in the KIT gene (which encodes the KIT protein, that influences cell proliferation, survival, and migration).[4]

Benign dermal naevi (moles) commonly contain a mutation in the BRAF gene, which may initiate melanomagenesis.[79] A recent meta-analysis estimated that 29% of CMM arose from a pre-existing nevus, with the remaining 71% arising *de novo*.[76]

In the Cancer Genome Atlas network, over 75% of CMM samples sequenced possessed a UV-signature in their mutation load (reviewed in[83]). In a recent study, CMM had the highest median number of mutations among 22 cancer types profiled,[1] with a high proportion of UV-signature mutations, and one of the highest rates of mutation per megabase, second only to squamous cell carcinoma (SCC) of the skin.[17] UV-induced mutations in genes encoding key proteins that protect the skin from UV-induced DNA damage, e.g., *TP53* (tumour suppressor factor p53 gene),[1] or the melanocyte response to UV radiation, e.g., *MITF* (microphthalmia-associated transcription factor gene), play an important role in melanomagenesis.[2]

Epigenetic alterations to DNA (e.g., methylation of a cytosine nucleotide) or chromatin (through histone modification), change gene expression without a change in the DNA base sequence.[66] A subset of CMM has been described that has elevated global DNA methylation and hypermethylation at specific cytosine guanine (CpG) dinucleotides in genes that are particularly involved in chromatin remodelling.[15] This subset was not clinically different from CMM without such changes.[15] Epidermal melanocytes are derived from neural crest progenitor (NCP) cells. In a zebrafish model, some NCP cells appeared to be epigenetically primed to become cancerous; i.e., the process of melanomagenesis may begin in melanocytes very early in life.[66]

There is growing interest in and research on the role of microRNAs (miRNA) in the development of CMM and disease progression. These are short (22–25 base pairs) non-coding RNAs that have actions in silencing and post-transcriptional regulation of gene expression. **Table S-1** outlines some of the miRNAs implicated in CMM. Profiling of miRNA expression may have prognostic value for CMM, for example for metastasis to the brain.[66] To date, much of this work derives from studies in mice or CMM cell lines, but the research is providing new insights into pathogenic pathways, and thus therapeutic interventions.

Table S-1 **Micro-RNAs implicated in CMM**

Micro-RNA	Evidence of association with CMM
miRNA-21	Upregulated in CMM and more highly expressed in CMM and metastatic melanoma than in dysplastic nevi; overexpression of miRNA-21 may be oncogenic and play a key role in development of CMM.[19]
miRNA-26a	Suppresses the growth and invasiveness of CMM cells.[82]
miRNA-106b5p	Acts as a promoter of CMM progression.[18]
miRNA-125b	Appears to inhibit proliferation and invasion of CMM cells, thus playing an important role in progression and metastasis.[19]
miRNA-137	Inhibits growth and migration of CMM cells[78]; downregulates expression of *MITF* (the master regulator of melanocyte development). Action is primarily as a tumour suppressor; lower expression is associated with poorer prognosis.[19]
miRNA-138	Promotes cell autophagy and apoptosis, and inhibition of cell proliferation.[63]
miRNA-203	Most highly expressed in human skin. Upregulation of miRNA-203 inhibits CMM cell migration; loss of expression is associated with greater tumour thickness and poorer prognosis.[19]
miRNA-211-5p	Induces activation of the survival pathway in CMM cells.[57]
miRNA-214	Also called 'melano-miRNA'; may facilitate metastasis by promoting cell migration, invasion and extravasation.[19]
miRNA-625	Appears to have tumour suppressive actions that inhibit the development and progression of CMM.[25]

Long non-coding RNAs (lncRNA, > 200 bp) may also have a role in CMM; for example, the lncRNA, NKILA, suppresses growth of CMM via regulation of the NF-kappa-β pathway.[7]

2.2 Diagnosis, treatment, and mortality in cutaneous malignant melanoma

The considerable research on the pathogenesis of CMM has led to advances in diagnosis and treatment. For example, diagnosis has progressed from visual inspection of characteristics of a skin lesion, through dermoscopy, and more recently to the use of genetic markers[84] and artificial intelligence to diagnose and classify skin lesions using deep neural networks.[23]

The advent of immunotherapy and checkpoint blockade treatment for CMM has led to reduction of tumour size and improved survival.[47] CMM cells express co-inhibitory molecules that are able to hijack the body's immune response to the tumour. Checkpoint blockade therapies prevent the interaction between these co-inhibitory molecules and their receptors, thus enabling the body's natural immune responses against the tumour.

3 Keratinocyte cancer

3.1 Pathogenesis of keratinocyte cancer

Most basal cell carcinomas (BCCs) arise because of mutations in genes in the hedgehog pathway that controls cell division and growth. This pathway is activated when sonic hedgehog protein binds to the Patched 1 protein (PTCH1), leading to loss of PTCH1 activity, and activation of the seven-transmembrane-span receptor protein (SMO).[37] This in turn results in upregulation of cell proliferation genes.

A small number of people inherit *PTCH1* mutations, leading to Gorlin's syndrome (also called basal cell naevus syndrome), which is characterised by early age of onset of BCC and a high incidence of multiple BCCs. In recent genetic profiling of 293 BCCs, up to 85% had alterations in components of the hedgehog pathway; 85% also had driver mutations in other tumour-related genes, including the *TP53* and *PTPN14* tumour suppressor genes, and the *MYCN* oncogene. Over 90% of single-nucleotide variants were of a UV-signature type (particularly C to T changes), underscoring the role of UV radiation in the pathogenesis of BCC.[9]

The most frequently identified gene mutations in sporadic SCC are inactivating mutations of the *TP53* tumour suppressor gene, with up to 50% of tumours affected. Other frequent mutations are in *CDKN2a* (which encodes two different tumour suppressor genes), *NOTCH1* (involved in regulating genes involved in differentiation, proliferation and apoptosis) and *TERT* (which encodes a component of the telomerase enzyme).[27]

3.2 Keratinocyte cancers and human papilloma virus

Meta-analyses have concluded that human papilloma virus (HPV) is significantly more likely to be found in SCC tumour tissue compared with normal skin, and that markers of HPV infection are associated with increased risk of SCC in immunocompetent people.[16] The significantly greater risk of SCC in organ transplant recipients compared with individuals without transplants, may be attributable to infection with HPV. A recent cohort study in organ transplant recipients found a modest increase in risk of SCC associated with the presence of 5 or more beta-HPV types in eyebrow hair follicles or a high viral load.[10]

Although these epidemiological findings suggest a role of HPV in SCC, it is not clear that this is causal. Many studies have been case-control in design, and it is possible that the presence of SCC in cases increased the risk of HPV infection or replication. In addition, many SCCs do not harbour detectable virus and the virus does not integrate into the host DNA, suggesting that, if HPV does influence the aetiology of SCC, it is via a different mechanism to infection with mucosal HPV types. Alternatively, UV-induced immunosuppression may have increased the risk of both SCC and HPV infection, despite there being no causal link between the two. However, in a recent cohort study, higher HPV load was associated with significantly higher (subsequent) incidence of SCC compared with low load or absence of HPV in eyebrow hair.[10]

Experimental models suggest a hit-and-run mechanism, in which viral oncogenes potentiate the accumulation of UV-induced DNA lesions (probably through inhibition of DNA repair and/or apoptosis) in crucial genes associated with SCC in humans. However, silencing of the viral oncogenes does not affect further tumour growth.[95] Most experimental studies have been

conducted in transgenic or experimentally infected models, so their relevance to humans is not clear. To overcome this, a rodent model, has been developed *(Mastomys coucha)* in which infection with *Mastomys natalensis* papillomavirus (MnPV) occurs naturally. The animals spontaneously develop benign and malignant skin tumours (SCC) that are histologically similar to lesions found in humans. In this model, MnPV and UV radiation at doses achievable by humans act synergistically to cause SCC, and the viral DNA is lost as tumours became malignant.[40]

4 Uveal melanoma and exposure to UV radiation

There remains little direct evidence of an association between uveal melanoma (UM) and exposure to UV radiation. Incidence decreases from the north to the south in Europe (four-fold higher in Norway and Denmark than Spain and northern Italy[46]) and in the USA (nearly five-fold higher incidence at latitude 47–48°N compared to 20–22°N[103]). In a recent meta-analysis, there was no evidence of an association between surrogates of exposure to UV radiation (for example, outdoor leisure activity and occupational exposure to sunlight) and UM. However, there was a nearly three-fold increase in risk of developing UM in association with the presence of atypical cutaneous naevi, and a significant increase in risk associated with presence of iris naevi, cutaneous freckles, a greater number of common naevi, light eye colour (blue or grey), and a tendency to sunburn.[72] UV-signature mutations are less common in UM than conjunctival or cutaneous melanoma, and explain less than 5% of the UM population-specific risk.[85] It seems unlikely that exposure to UV radiation is a major risk factor for UM, with evidence more in keeping with an increased risk in relation to what are recognised as markers of a sun-sensitive phenotype.

5 Possible mechanisms of action of vitamin D in human disease

The active form of vitamin D, $1,25(OH)_2D$, has effects through both genomic and non-genomic pathways. Genomic actions are mediated by binding to a nuclear vitamin D receptor (VDR).[8] After activation by $1,25(OH)_2D$, the VDR binds to DNA sequences to modify transcriptional output. Rapid, non-genomic effects also involve binding to a membrane VDR or a membrane-associated rapid response steroid binding protein.[8] The effects of $1,25(OH)_2D$ in maintaining calcium metabolism occur through upregulation of intestinal absorption, and reduction in renal loss, of calcium and phosphate, and possibly through direct effects on cartilage and bone.[8] A wide range of cell types possess nuclear VDRs, including adipocytes, pancreatic β cells, cardiac myoctes, and immune cells. Experimental studies show that $1,25(OH)_2D$ promotes lipogenesis and insulin secretion, and is anti-proliferative, stimulates repair of DNA damage, and inhibits tumour angiogenesis and metastasis.[8] In the skin, topical $1,25(OH)_2D$, or therapeutic analogues, inhibit proliferation, stimulate differentiation, and suppress immune activity; they may thus be of value in disorders with an underlying basis in excessive proliferation and lack of differentiation, such as psoriasis and skin cancers.[8]

6 Phototherapy to treat human diseases

UV radiation is a potent modulator of human skin disease. Whereas it causes photosensitivity and photo-aggravation in many people, phototherapy with UV radiation is also beneficial in a range of skin conditions, including psoriasis, atopic dermatitis and vitiligo.[3, 39] Seemingly paradoxically, certain photosensitivity disorders, including polymorphic light eruption, can also benefit from phototherapy.[98]

Narrowband UV-B (peak 311–312 nm) is a popular form of phototherapy,[3] while broadband UV-B (280–320 nm) and psoralen-UV-A (PUVA)[56] are also used. UV-A1 (340–400 nm) phototherapy is effective in atopic dermatitis, localised scleroderma and systemic lupus erythematosus,[49] and is under exploration in conditions particularly involving the deeper (dermal) skin layer.

Psoriasis is a chronic autoimmune disease characterised by hyper-proliferation and inflammation of the skin. Phototherapy reduces the T-cell mediated inflammation in psoriasis, including downregulating Th-17 cell activity, while upregulating immunosuppressive cytokines including IL-10,[70, 99] and restoring the numbers of regulatory T cells (T_{reg}).[28] The latter may be responsible for the prolonged remissions that are frequently seen in psoriasis following phototherapy.[39, 96]

In atopic dermatitis, there is impairment of the skin barrier and enhanced susceptibility to allergens, bacterial colonisation and infection, in addition to dysregulation of the skin immune system, thus providing many possible targets for phototherapy.[39] Narrowband UV-B phototherapy is reported to reduce the activity of the Th-2 and Th-22 axes, and to a lesser extent the Th-1 axis, in atopic dermatitis,[91, 93] with reduction in IL-22 correlating with improvement in clinical activity scores.[93] Narrowband UV-B treatment of atopic dermatitis may also operate through an antimicrobial effect, modulating AMP,[29] and reducing microbial carriage and exotoxin production.[89] Furthermore, UV irradiation assists the normalisation of the epidermal barrier.[43, 93] In contrast to psoriasis, remission with phototherapy is usually short in atopic dermatitis, which may be explained by residual genomic changes and sub-clinical inflammation.[91]

Rising temperatures and changes in humidity as a result of climate change have been hypothesised to alter the severity of atopic dermatitis and its associated itching.[73] Nevertheless, the challenges of separating out different climatic effects, and the reliance largely on ecological (correlation) effects, make any predictions highly speculative at this time.

Vitiligo occurs through autoimmune destruction of melanocytes, with involvement of cytotoxic T cells,[94] producing well-delineated white skin patches. It is the commonest depigmentation disorder, estimated to occur in 0.4–2% of the world's population.[21] It produces high psychological morbidity especially in those with darker skin types. Narrowband UV-B phototherapy is an effective treatment for vitiligo; the mechanisms of its action in this skin disease fall into 2 major areas.[39] Firstly, UV-B irradiation promotes the proliferation, differentiation and migration of melanoblasts and melanocytes, which move outwards from their immune-privileged site in the hair follicle bulge to the inter-follicular epidermis.[34] Secondly, several immunoregulatory properties of UV-B irradiation are anticipated to operate, including apoptosis of cytotoxic T cells. Reduction in IL-17 and IL-22 levels and increased T_{regs} are reported following narrowband UV-B phototherapy, with correlation of these changes to improved scores of vitiligo clinical activity.[42]

7 Health-related "side effects" of fears about stratospheric ozone depletion and the Montreal Protocol

7.1 Sunbeds – history and demise

The first sunbed – the incandescent light bath – was developed in 1891 by John Harvey Kellogg (the inventor of Corn Flakes) as an *"aid to good health"*.[64] In 1903, Finsen was awarded the Nobel Prize for medicine for his work on phototherapy, and during the early 20th century sun baths and sunlamps were used for their purported health benefits, for example, for skin conditions. In 1975, a German scientist developed and patented the tanning bed, emitting 95% UV-A and 5% UV-B, at a time when a tan was becoming fashionable.[64]

There are no analyses of possible links between recognition of stratospheric ozone depletion and the growth in interest in indoor tanning. However, it is conceivable that the recognised threat of large increases in ground level UV-B radiation as a result of ozone depletion and ensuing concerns about the high risk of skin cancer,[20] alongside the social desirability of a tan, may have led to what was perceived as a safer form of tanning – sunbeds. Whatever the underlying reasons (and no doubt driven by commercial interests), the number of sunbeds and the number using them rapidly increased over the latter years of the 20th century.[68]

By the early years of the 21st century, across Australia, Europe, and the USA, 14% of the general population of adults, 43% of university students, and 18% of adolescents had tanned indoors in the previous year.[97] In the USA in 2010 there were ~30 million indoor tanners[53] using ~25,000 indoor tanning facilities. In the UK there were 5350 tanning salons in operation in 2009, including 484 in Scotland.[35] In many countries, statistics on the number of tanning beds are not available, as no registration is required.

In 2009, the International Agency for Research on Cancer (IARC) classified tanning devices as carcinogenic to humans.[22] A systematic review of measurements of UV radiation in indoor tanning devices showed that typical values were higher than those from natural solar radiation and that there was wide variation between devices. The erythema-weighted UV irradiances were highest in the most recent studies (see **Fig. S-1**).[75] In particular, UV-A irradiances were very high in some devices, far exceeding solar levels.

Sunbed use has been linked to an increased risk of CMM, with the strongest risk for first exposure to indoor tanning before age 30 years.[30] A recent systematic review has challenged this view, on the basis that studies are generally of low quality and with high risk of bias.[13] Of note, a recent study showed that people who frequently used sunbeds also reported never or seldom using sun protection when outdoors.[26] This highlights the difficulty of separating indoor from outdoor tanning, and thus providing high quality evidence that indoor tanning causes CMM. Nevertheless, the precautionary principle suggests control is required for this extraneous source of high dose UV radiation used for purely cosmetic purposes.

Additionally, there is risk of harm to the eye during sunbed use through insufficient provision and/or use of protective eyewear – this is of particular concern in young people owing to the immaturity of the lens and hence its greater transmission of solar radiation in UV wavelengths.[71]

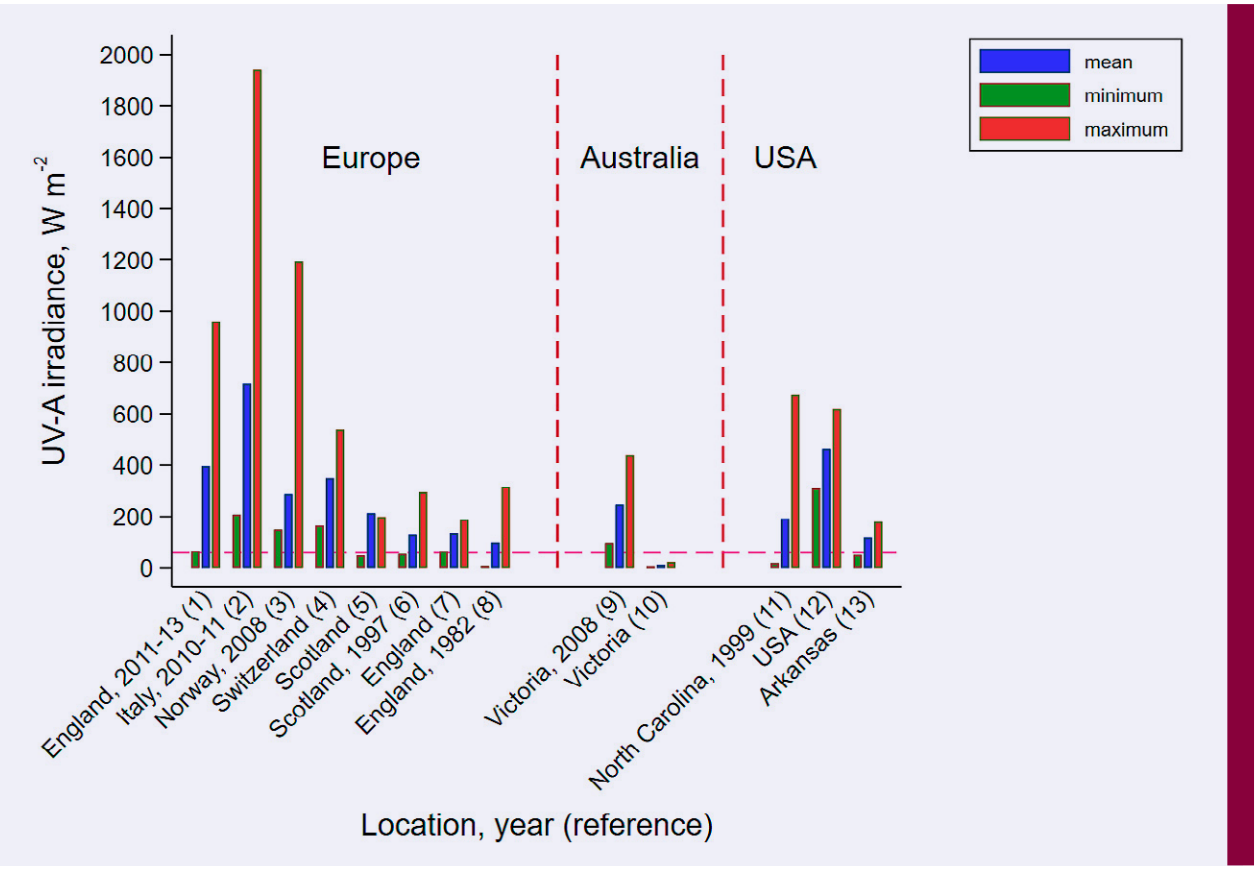

Fig. S-1 **UV-A irradiance in tanning beds around the world. Data from.[75] Pink horizontal dotted line represents natural solar UV-A irradiance at midday in the tropics. References: 1[50]; 2[24]; 3[74]; 4[31]; 5[67]; 6[60]; 7[101]; 8[11]; 9[33]; 10[32]; 11[44]; 12[65]; 13[12].**

Control of sunbeds began in 1997, when France banned indoor tanning for minors. The World Health Organization maintains a database of national regulations on access and control of sunbeds;[100] examples of control legislation are provided in **Table S-2.**

An Australian study monitoring advertisements on Gumtree and e-Bay to sell sunbeds or seeking access to a sunbed, found a reduction in units for sale following the ban on sunbeds and an increase in the price sought, but an increase in the 'access wanted' advertisements.[90] Ongoing monitoring of possible illegal or 'underground' use of sunbeds is recommended to ensure the health benefits of banning sunbed use.

Table S-2 **Regulation of sunbed use in selected countries, including by age where relevant.**

Country	Control status
Brazil	Banned for < 18 years in 2002; complete ban, 2009
Australia	Complete ban all states and territories, 2016
New Zealand	Ban for < 18 years, Jan 2017
Scotland	Ban for < 18 years, 2009

Country	Control status
Belgium	Banned for < 18 years, 2009; from 2019 every user will need a unique electronic pass to log on to control use by minors and a first-time user must have a skin type certificate from a medical doctor
Norway	Banned for < 18 years, July 2012; from Jan 2017 all tanning studios must have an age control system
Denmark	No age limit
Sweden	Banned for < 18 years, Sept 2018
Canada	Banned for < 18 years in British Columbia (Oct 2012), Alberta (Jan 2018), Manitoba (Jan 2016), Saskatchewan (Nov, 2015), Ontario (Oct 2013), Quebec (Feb 2011), Prince Edward Island (Sep 2013); for < 19 years in New Brunswick (Jun 2013), Nova Scotia (May 2011), Newfoundland and Labrador (Jun 2012), and the Northwest Territories (Mar 2013)
USA	Banned for < 18 years in California, Delaware, District of Columbia, Hawaii, Illinois, Kansas, Louisiana, Massachusetts, Minnesota, Nevada, New Hampshire, North Carolina, Oregon, Texas, Vermont, Washington, Jan 2017

7.2 Growth of research

An upsurge in research that followed the Montreal Protocol, has been important in discovering the mechanisms underlying UV-induced skin cancer, and has thus led to the development of new therapeutic agents and diagnostic tools. The development of new apps for monitoring personal sun exposure, and monitoring devices for use in research are discussed above, and in Chapter 1. In addition to these electronic tools, novel biomarkers of acute or chronic sun exposure are being developed for use in research studies (see also[51]). These advances are discussed below.

7.3 Biomarkers of sun exposure

Conjunctival UV autofluorescence (CUVAF) photography was developed to detect and quantify UV-induced damage on the surface of the eye.[45] Eyes with pterygia have larger areas of CUVAF,[61, 88] while myopic eyes have less.[62, 87] Greater CUVAF area is associated with older age, greater proportion of the day spent outdoors while working,[41] and less frequent use of sunglasses, in adults.[48] Larger CUVAF areas were measured in Caucasian children with lighter skin pigmentation, eye and hair colour, increased number of lifetime sunburns, freckling by the end of previous summer, and less use of sunhats.[92]

Iris freckles are dark spots on the coloured part of the eye (iris), formed by the accumulation of cells containing melanin. They do not have malignant potential but seem likely to indicate a high cumulative dose of UV radiation, as well as constitutive sensitivity to the sun.[86] Iris freckles are more common with increasing age, lighter eye colour, greater lifetime number of sunburns and severe sunburns, and not using sun protection. Thus, they may have use as markers of the biological dose of UV radiation to the eye.

Skin surface topography, using silicone impressions of the back of the hand, has been used for some years to measure cumulative exposure to UV radiation and photoageing.[5] Recent techniques in digital analysis of the silicone impressions may provide much finer-grained scoring allowing more precise tracking of changes over time.[52]

The assessment of DNA photodamage in the skin requires the taking of a biopsy, which is not suitable for large-scale screening. Most DNA lesions are repaired by nucleotide or base excision repair and some of the excision fragments can be detected in urine; this offers the potential for assessment of DNA damage in research studies.[54] However, at present there are no techniques that are economically suitable for large-scale use. An alternative possibility is the use of a suture-free and minimally-invasive microbiopsy.[55]

A positive correlation between self-reported personal sun exposure and the frequency of micronuclei and demethylation in long interspersed nucleotide elements (LINE-1) in peripheral blood lymphocytes suggests that these changes may allow an objective assessment of exposure to UV radiation.[69] These changes may represent useful markers in exploring pathogenetic pathways, but expense currently precludes their common use.

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3 Linkages between stratospheric ozone, UV radiation and climate change and their implications for terrestrial ecosystems

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Summary

Exposure of plants and animals to ultraviolet-B radiation (UV-B; 280–315 nm) is modified by stratospheric ozone dynamics and climate change. Even though stabilisation and projected recovery of stratospheric ozone is expected to curtail future increases in UV-B radiation at the Earth's surface, on-going changes in climate are increasingly exposing plants and animals to novel combinations of UV-B radiation and other climate change factors (e.g., ultraviolet-A and visible radiation, water availability, temperature and elevated carbon dioxide). Climate change is also shifting vegetation cover, geographic ranges of species, and seasonal timing of development, which further modifies exposure to UV-B radiation. Since our last assessment, there is increased understanding of the underlying mechanisms by which plants perceive UV-B radiation, eliciting changes in growth, development and tolerances of abiotic and biotic factors. However, major questions remain on how UV-B radiation is interacting with other climate change factors to modify the production and quality of crops, as well as important ecosystem processes such as plant and animal competition, pest-pathogen interactions, and the decomposition of dead plant matter (litter). In addition, stratospheric ozone depletion is directly contributing to climate change in the southern hemisphere, such that terrestrial

ecosystems in this region are being exposed to altered patterns of precipitation, temperature and fire regimes as well as UV-B radiation. These ozone-driven changes in climate have been implicated in both increases and reductions in the growth, survival and reproduction of plants and animals in Antarctica, South America and New Zealand. In this assessment, we summarise advances in our knowledge of these and other linkages and effects, and identify uncertainties and knowledge gaps that limit our ability to fully evaluate the ecological consequences of these environmental changes on terrestrial ecosystems.

1 Introduction

The structure, function and diversity of terrestrial ecosystems are being modifed by ongoing changes in the Earth's climate, and these complex changes are becoming increasingly evident with time.[149, 257, 319] An assessment of the effects of depletion and recovery of stratospheric ozone and associated changes in ultraviolet-B radiation (UV-B, 280–315 nm) on the terrestrial biota must, therefore, consider the role of climate change in the response of these organisms and ecosystems. In some regions, stratospheric ozone depletion is itself contributing to climate change with the result that ecosystems are being affected by the consequent ozone-driven changes in temperature and precipitation (see Chapter 1 and ref.[273]). Prior assessments have considered the effects of stratospheric ozone depletion in the context of climate change and have reported on some of the ways in which climate change can potentially interact with ozone depletion and UV-B radiation to modify terrestrial ecosystem function and composition.[26, 50, 61] Here, we report on progress made since the last Assessment.[50] and examine and further explore recent findings that document interactive effects of ozone depletion, UV-B radiation and climate change on terrestrial organisms and ecosystems, including cultivated species and highly managed ecosystems (e.g., agro-ecosystems). We emphasise effects that have, at least to some degree, been demonstrated to occur in nature, but also identify areas where potential effects on terrestrial ecosystems could occur in the future. Where possible, areas of uncertainty are addressed, and the significance of findings is placed in a context relevant to policy makers.

Ecologically significant linkages between stratospheric ozone depletion, climate change and UV radiation are diverse, sometimes bi-directional, and, in certain cases, exhibit important feedbacks to the climate system (**Fig. 1**). However, climate change is increasingly contributing to changes in the timing and duration of UV-B radiation exposure, independent of changes in stratospheric ozone. These changes can occur in a number of ways (see section 7). One avenue involves climate change-driven shifts in cloud cover, which is increasing in some regions (usually wetter areas), while decreasing in others (usually drier regions) see Chapter 1 and ref.[149] Similarly, climate change-driven effects on vegetation (e.g., forest die-back or shrub invasions) can increase or decrease the UV exposure conditions of understory plants and animals. As a result of warmer growth conditions and altered timing of seasons, many plants are initiating growth and flowering earlier in the year,[74, 170] while certain animals are adjusting their timing of breeding and migration.[53, 311] As UV-B radiation varies seasonally (Section 7.2), a change in the timing of important life-cycle events can easily affect their exposure to UV-B radiation. In addition, the geographic ranges of many plants and animals, including wild and domesticated species, are shifting to higher elevations and latitudes in response to climate change.[149, 253, 257, 291, 299] Because of existing natural altitudinal and latitudinal gradients in solar UV radiation (see Chapter 1 and refs[48, 62, 226]) these changes in

geographic ranges can potentially increase (at high elevations) or decrease (at high latitudes) the amount of UV-B radiation received by organisms. Unlike ozone depletion, all of the above climate change-driven effects are modifying exposure of organisms to the full solar radiation spectrum at the Earth's surface, including UV-B as well as UV-A (315–400 nm) and visible (400–700 nm) radiation. At the same time, plants and animals are being exposed to novel combinations of UV radiation with other abiotic (e.g., changing day length, and fluctuating temperatures) and biotic factors (e.g., competitors, pests, and pollinators). Because of these complexities, it is necessary to consider how responses of organisms and ecosystems to UV-B radiation are modified by concomitant changes in other regions of the solar spectrum (i.e., UV-A and visible radiation) as well as simultaneous changes in a diverse range of abiotic and biotic factors.

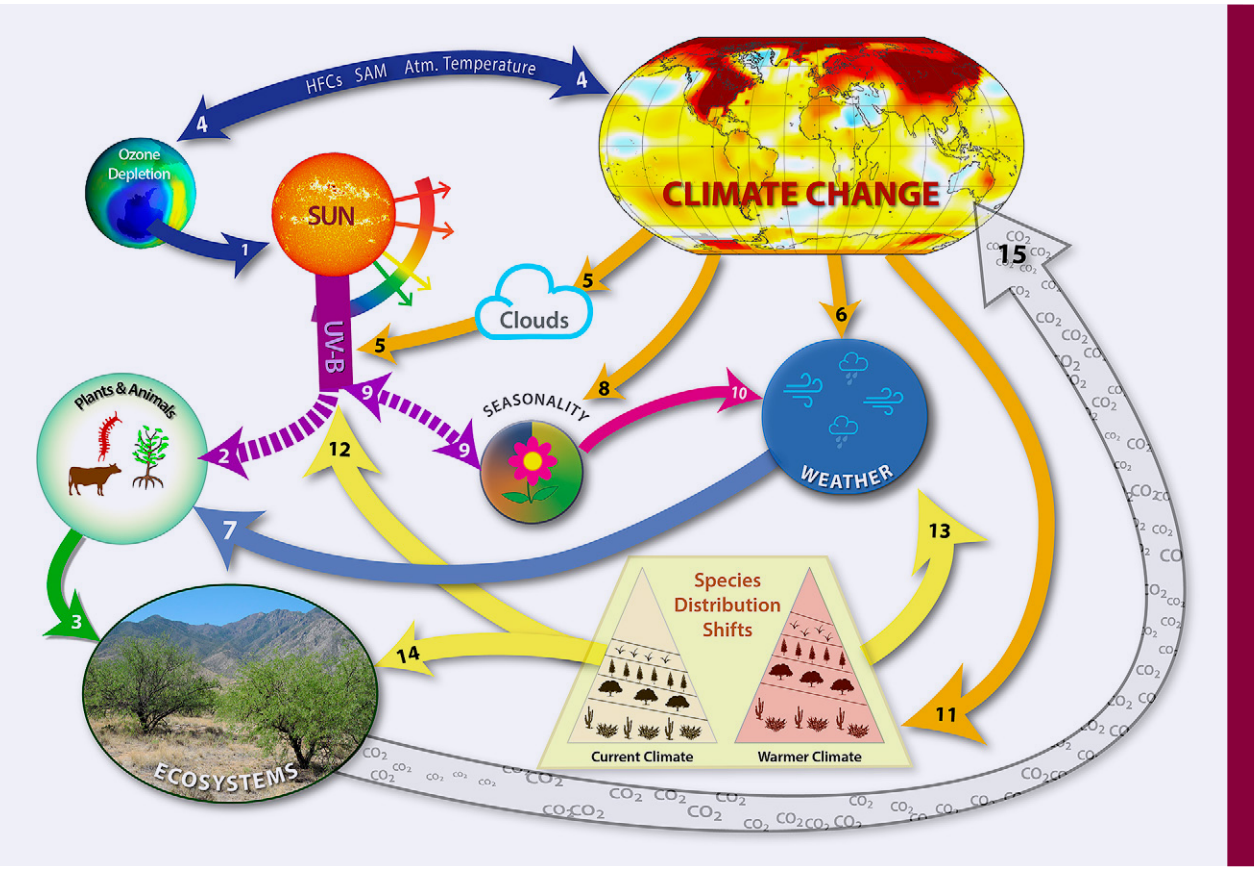

Fig. 1 **Conceptual diagram illustrating known linkages between stratospheric ozone depletion, UV radiation and climate change on terrestrial organisms and ecosystems. Stratospheric ozone depletion alters UV radiation (primarily UV-B; arrow 1), which in turn directly affects plants and other organisms (arrow 2). The effects on organisms can then alter the function and structure of ecosystems (arrow 3). Ozone depletion can alter the climate, and climate change can affect ozone depletion via several avenues (arrow 4). Certain ozone-depleting substances (e.g., hydrofluorocarbons (HFCs) and others) are potent greenhouse gases that can enhance global warming. Stratospheric ozone depletion in the southern hemisphere is directly altering climate via changes in the Southern Annular Mode (SAM) in addition to other climate changes. Resultant shifts in climate zones alter regional rainfall and drought and thereby change cloud cover; in turn, the changing cloud cover can increase or decrease exposures of organisms to UV radiation (arrow 5). Climate-related changes in weather patterns (arrow 6) alter temperature**

and precipitation patterns, which can directly modify plant growth and development, and the way in which plants respond to UV-B radiation (arrow 7). Climate change (including altered UV-B exposure) is also changing the seasonal timing of development (e.g., phenology of flowering or bud break; arrow 8), such that wild plants and crops develop at times of the year when UV radiation can be either greater or less than prior to current rapid climate change (arrow 9). These phenological changes further expose plants to novel combinations of UV radiation and other abiotic and biotic factors (arrow 10). In response to climate change many organisms are shifting their ranges to higher elevations and latitudes (arrow 11). As with phenological shifts, these changes in geographic ranges can potentially increase (elevation) or decrease (latitude) exposures to UV radiation (arrow 12), as well as subjecting organisms to new combinations of UV radiation and other abiotic factors (arrow 13). As species migrate to different environments they also encounter new combinations of competitors, pests and pollinators that may alter important ecosystem processes such as herbivory and competition (arrow 14). Alterations in certain ecosystem processes, such as decomposition, can modify soil carbon storage and emissions of carbon dioxide and other greenhouse gases to the atmosphere (arrow 15). Image of stratospheric ozone shows total ozone over Antarctica (October 2017, Source: https://ozonewatch.gsfc.nasa.gov). Climate change map indicates surface temperature anomalies for February 2017 compared to the base-period of 1951–1980 (Source: https://data.giss.nasa.gov). Sonoran desert ecosystem photograph by P.W. Barnes.

Solar UV radiation (UV-B and UV-A) is known to affect the growth and performance of terrestrial plants and animals (see sections 3 and 4). The shorter wavelengths of UV radiation (mostly in the UV-B range) may cause cellular damage, which can lead to changes in the morphology, physiology, and biochemistry of the organism. However, concurrent exposure to longer wavelengths (e.g., UV-A and/or visible radiation), can often reduce the negative effects of UV-B radiation.[322] In addition, both UV-B and UV-A radiation are important sources of information for plants and animals. This radiation is perceived by specific photoreceptors, which trigger a range of responses. Many animals sense UV radiation and avoid exposure to prolonged periods of high UV-B radiation.[81, 222] These behavioural responses together with physiological mechanisms can mitigate some of the negative outcomes of high UV-B radiation. In some animal species (e.g., insects and birds), UV radiation is used as a visual cue that enhances foraging, mate selection, or other behavioural activities.[81] By comparison, land plants are sessile (rooted to their growth medium) and require sunlight for photosynthesis and growth. Their primary response to changing UV radiation conditions typically involves acclimating or adapting to these changes using biochemical and physiological mechanisms. However, like animals, plants can sense UV radiation in their surroundings, which has adaptive value.[159]

Following the discovery of the Antarctic ozone hole, many initial studies (as reviewed in refs [11, 32, 46]) emphasised the direct detrimental effects of increased UV-B radiation on plants, especially important food crops. However, most evidence to date indicates that, under realistic exposures, the direct, damaging effects of high UV-B radiation on photosynthesis, plant productivity and crop yield, are relatively minor.[26, 110, 155, 240, 283, 336] More recent studies have focused on understanding how plants a) respond to UV radiation against the backdrop of a rapidly changing climate in conjunction with current and projected stratospheric ozone dynamics; and b) perceive the UV-B radiation and what role this radiation plays in regulating growth and development.[44, 160, 162, 356] At present, it is widely accepted that UV-B radiation can have beneficial as well as unfavourable effects on plants.[156, 208, 239, 336] In some cases, reduced exposure to UV-B radiation can even have negative consequences for plant growth, defence against pests,[27] and food quality.[20] Thus, projected recovery of stratospheric ozone to levels that may exceed those in the recent past (i.e., 1970's; Chapter 1 and ref.[256]), means that there

is a need to fully evaluate how organisms and ecosystems will respond to the increases *and* decreases in solar UV-B radiation that occur in conjunction with a rapidly changing climate.

Climate change alters regional weather patterns, including temperature and precipitation, and these changes can directly affect plants and ecosystems by altering moisture availability and critical thermal conditions for growth, reproduction, and survival. Of interest in this assessment, however, is how plant responses to climate change are modified by UV radiation (see section 3). Exposure to UV-B radiation can enhance plant tolerance to some abiotic factors (e.g., water and temperature stress),[275] while other factors may alter the sensitivity of plants to UV radiation. However, these effects are complex and often dependent upon specific growth conditions.[217] Understanding how plants respond to changes in UV radiation against this backdrop of changes in multiple environmental variables is thus challenging but necessary in the context of future environments (e.g., ref.[326]). These UV-climate change interactions are particularly relevant for agroecosystems, where changes in crop yield, food quality, resistance to pests and diseases, and overall vulnerability of plants to climate change can have significant impacts on food security (see section 5).

The effects of changes in incident solar UV radiation (UV-B and UV-A) on ecological communities and ecosystems are largely a consequence of impacts on primary producers (i.e, plants).[25, 63, 335] These higher-level ecological effects include changes in plant-plant interactions (competition), herbivory, pest-pathogen interactions and the decomposition of dead plant matter (litter) (see section 6). Although initially minor, some of these community- and ecosystem-effects may accumulate over time (e.g., ref.[276]) or be amplified by processes such as competition.[37] For certain crop species, exposure to UV radiation can elicit changes in pest/pathogen defence that may have positive consequences for the productivity and sustainability of agroecosystems.[25, 27, 335]

One important ecoystem-level effect of changes in UV radiation and climate is the altered decomposition of plant litter, which can result in a positive feedback to the climate system, thereby contributing to climate change. Photodegradation is the process whereby UV radiation, together with shorter wavelengths of visible radiation, drives the photochemical break-down of plant litter, and this results in the release of carbon dioxide and other gases to the atmosphere (see section 6.3, Chapter 5 and refs [54, 181]). Photodegradation can also modify the chemical make-up of litter, thereby promoting or facilitating the activities of microbial decomposers (bacteria and fungi; i.e., photo-facilitation). This results in increased microbial and soil respiration, and contributes additional carbon dioxide to the atmosphere.[17, 22, 279] At present, considerable uncertainty remains regarding the quantitative significance of photodegradation of terrestrial plant litter, and its effects on storage of carbon in soil and concentrations of atmospheric CO_2. However, it is clear that this process is an important driver of decomposition in many ecosystems, especially drylands (grasslands, deserts, and savannas).[3, 17] In some of these dryland ecosystems, the relative importance of UV-driven photodegradation may increase with climate change as precipitation decreases and temperature increases.[5] Changes in climate and land-use may also affect photodegradation and litter decomposition indirectly via changes in the structure and species composition of vegetation, and occurrence of fire and soil erosion (see section 6.3 and Chapter 5).

There are several linkages between ozone depletion and climate change that are ecologically important but which do not directly involve changes in UV radiation. On the one hand, climate change can modify stratospheric ozone depletion by perturbing temperature dynamics between the stratosphere and troposphere.[13] Conversely, it is now apparent that stratospheric ozone depletion in the southern hemisphere is directly contributing to

climate change (**Fig. 2**) (see Chapter 1) Specifically, ozone depletion appears to be changing patterns of regional atmospheric circulation in the southern hemisphere which, in turn, affect weather conditions, sea surface temperatures, and frequency of wildfires.[75, 143, 171, 188, 248] These changes together with changes in UV-B radiation can have several consequences for terrestrial ecosystems (see section 2, **Table 1**, and ref.[273]). While ozone depletion in the northern hemisphere may be associated with similar, but smaller, climate shifts (Chapter 1), to our knowledge, there are no reports linking this to ecological impacts.

Finally, a better understanding of how terrestrial organisms and ecosystems might respond to changes in UV radiation in the context of modern climate change is coming from studies examining how plants and animals have adapted to changing UV radiation and climate conditions in the past. These historical studies, however, require some knowledge of how UV radiation has changed over geological time periods. In the absence of satellite or ground-based measurements of UV radiation, some investigators have attempted to reconstruct past UV radiation climates using biological indicators as proxies for ground-level UV radiation. Section 8 evaluates progress made in the development of pollen grains and spores as bioindicators of past UV conditions.

2 Ecological effects of ozone depletion on climate in the southern hemisphere

Stratospheric ozone depletion has led to large changes in the climate of the southern hemisphere (as detailed in Chapter 1 and refs[50, 273]). These are manifested in a mode of atmospheric variability, the Southern Annular Mode (SAM or Antarctic oscillation), which describes the difference in pressure between 60° and 45° S. The SAM describes the strength and latitudinal position of the westerly wind belt (i.e., jet stream) around Antarctica (see also refs[50, 273]). Ozone depletion is linked to a highly positive phase of the SAM,[2, 135] corresponding to an increased pressure difference between mid- and high latitudes and a contraction of the westerly wind belt towards Antarctica (**Fig. 2**). The effects of this change in atmospheric circulation, which extend across the southern hemisphere, are summarised in the following sections. The sections emphasise how these changes in climate link to stratospheric ozone depletion (see also Chapter 1), affect abiotic drivers (e.g., wildfires) and the contingent responses of southern hemisphere ecosystems. The implications of these climate shifts for marine and aquatic ecosystems are described in Chapter 4.

Changing concentrations of stratospheric ozone have been linked to changing surface temperatures, altered wind and ocean circulation patterns and changing precipitation patterns, causing increased rainfall or drought, the latter leading to increased risk of wildfires. As presented in our last assessment, terrestrial[50] and aquatic ecosystems[273] including biogeochemical cycling[103] have been affected by these changes across the southern hemisphere. Sections 2.1 and 2.2 give a brief summary of the climate changes ascribed to ozone depletion and then address the implications of these changes for ecosystems in the southern hemisphere.

The UNEP Science Assessment Panel (SAP)[346] notes that since their last assessment,[345] further research has confirmed the impact of changes in stratospheric ozone on the tropospheric and surface climate of the southern hemisphere and has, in some cases, allowed better quantification and attribution of the changes. Stratospheric ozone depletion is assessed to have been the dominant driver of changes in atmospheric circulation across the southern

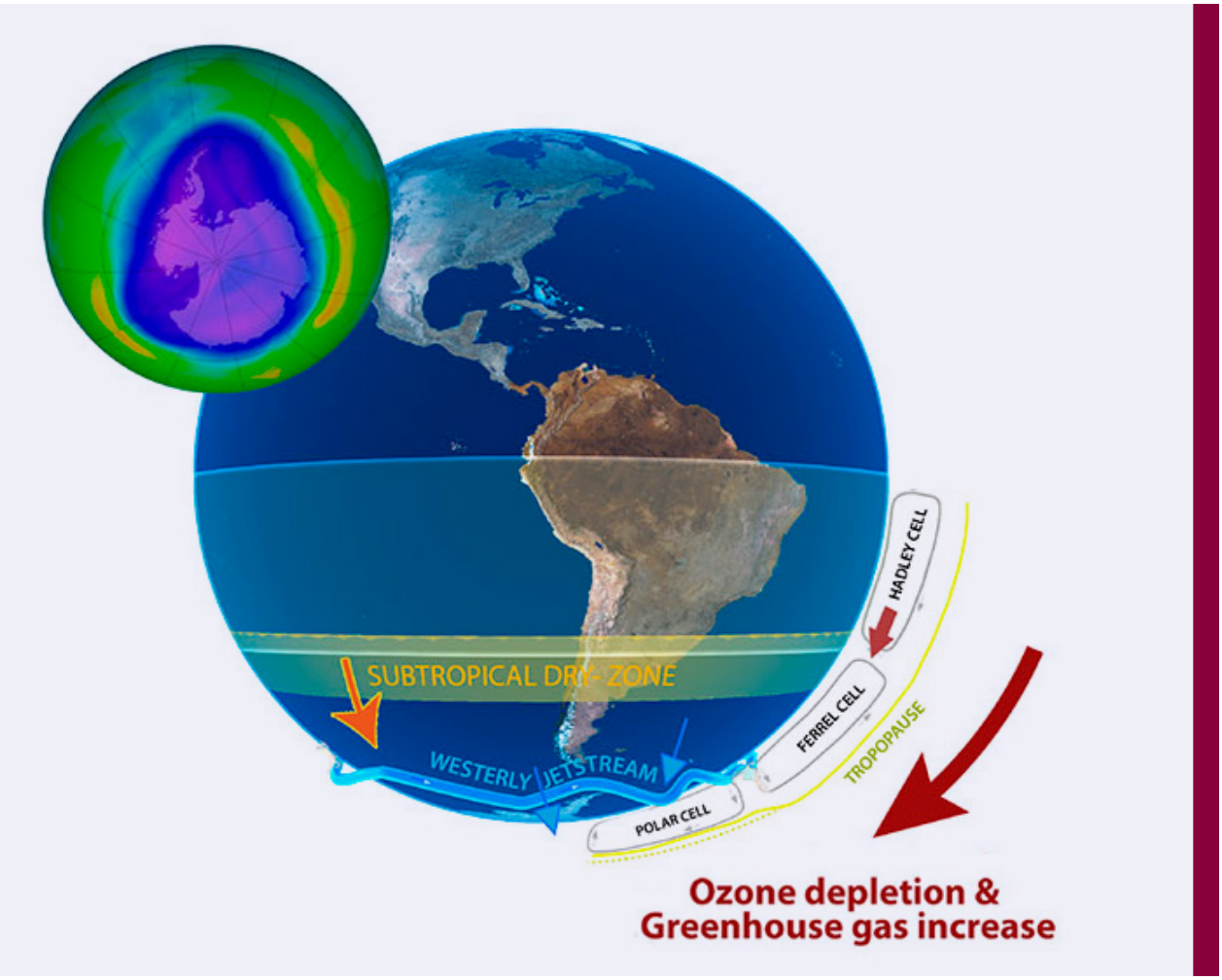

Fig. 2 **The Antarctic ozone hole (inset) and its impact on southern hemisphere atmospheric circulation. Stratospheric ozone depletion and resultant cooling over Antarctica has caused the tropopause to lift, allowing the Hadley Cell (dark red arrow) and the westerly jet stream to tighten and shift towards the South (blue arrow). The speed of the jet has also increased (see ref.[273] for details). The polar shift in the jet and its increased strength changes atmospheric and oceanic circulation throughout the southern hemisphere consistent with a more positive phase of the Southern Annular Mode (SAM; see text below for explanation). Over the past century, increasing greenhouse gases and then ozone depletion over Antarctica have both pushed the SAM towards a more positive phase, and the SAM index is now at its highest level for at least 1000 years.[2] As a result, high latitude precipitation has increased and the mid-latitude dry zone has moved south (orange arrow). As the ozone layer recovers, increased greenhouse gas forcing will likely take over and the position of the jet is thus predicted to remain in this more southerly location. Figure adapted from refs [258, 273], with ozone 'hole' over Antarctica, 17th September 2006, reproduced from NASA Ozone Watch.[236]**

hemisphere from the mid-latitudes to the tropics during austral summer (December-February) over the period 1960 to 2000 when stratospheric ozone was decreasing; while in other seasons, greenhouse gas emissions play a comparable role to stratospheric ozone depletion. As stratospheric ozone recovers, its effect on circulation should diminish; however, climate change is predicted to increasingly contribute to changes in atmospheric circulation Chapter 1 and refs [93, 294].

The major changes in mid-latitude and tropical circulations driven by stratospheric ozone depletion include the poleward shift of the mid-latitude jet (**Fig. 2**), the shift to an increasingly positive phase of the Southern Annular Mode (SAM) and the poleward shift of the sub-tropical Hadley Cell (**Fig. 2**).[20, 306, 346] Between 1980 and 2000, the westerly jet shifted south during summer by approximately one degree of latitude. Since 2000, the jet has shifted north in summer, although this reverse trend is not statistically significant.[151, 346] A meta-analysis[338] supports stratospheric ozone depletion as the dominant driver of the Hadley Cell summertime expansion over the period 1979 to late 1990s.

2.1 Changes to southern hemisphere regional rainfall related to stratospheric ozone depletion, and ecosystem responses to fluctuating availability of water, extreme rain, drought and fires

Changes in both extratropical and sub-tropical austral summer rainfall have previously been linked to the position of the mid-latitude jet and thus to stratospheric ozone depletion (**Figs 2, 3** and see Chapter 1 and refs [50, 69, 131, 273, 345]). South-East South America (northern Argentina, Uruguay, southern Brazil and Paraguay) has experienced one of the largest increases in rainfall worldwide (**Fig. 3**; **Table 1A**)[121] with a 30% increase in summer rainfall over the past 50 to 100 years. While this increased rainfall appears to be the result of anthropogenic emissions of greenhouse gases,[96, 320] the relative contributions from greenhouse gases and ozone depletion to these changes have not yet been resolved (see also refs [352, 359]).

The SAM has been identified as the leading cause of changes in summer rainfall, surface temperature, and the diurnal temperature range in East Africa[206, 207], and these authors highlighted the effects of stratospheric ozone depletion. Over the period 1961–1996, the position for the South Pacific Convergence Zone (a region of abundant precipitation, stretching from New Guinea towards southern hemisphere mid-latitudes) has changed, with increasing rainfall on the northern edge and decreases to the south.[58] This shift in precipitation appears related to concentrations of stratospheric ozone, with models suggesting a reversal of these effects as stratospheric ozone recovers.[58] These shifts in rainfall patterns can have negative and positive effects on ecosystems, populations and individual species.

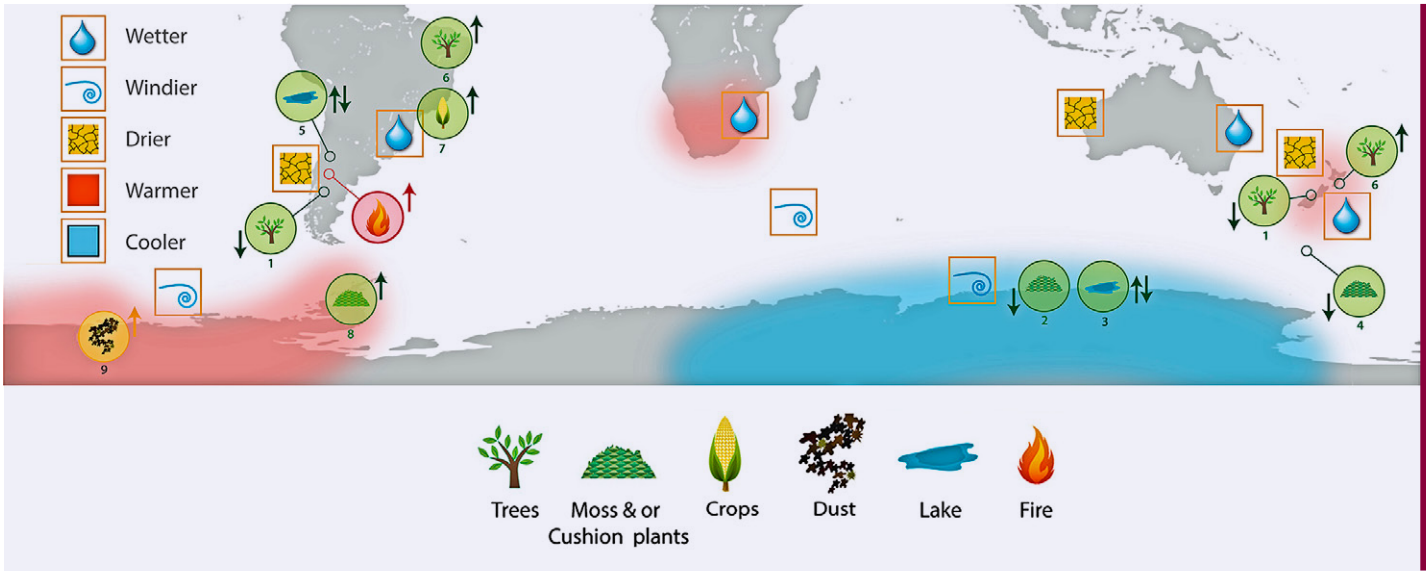

Fig. 3 Map of the southern hemisphere showing how stratospheric ozone depletion affects the climate and environment, and the effects of these abiotic changes on terrestrial ecosystems and populations. Symbols show types of organism, ecosystem or entity affected (see legend below figure), with numbers referring to Table 1 (C), which provide species and location details. Arrows indicate direction of effects on biodiversity, up = positive, down = negative effects, two-way arrows indicate changed biodiversity.

Table 1 How stratospheric ozone depletion affects the climate and environment: summarised according to (A) the likely consequences, (B) the effects of these abiotic changes on terrestrial ecosystems, and (C) populations affected across the southern hemisphere (itemised numerically matching locations in Fig. 3). Regions affected, and references are provided.

A. Changes in southern hemisphere climate driven by stratospheric ozone depletion	Regional examples	References
Changing regional precipitation		Chapter 1 and refs [19, 93]
Wetter	• South East South America (Northern Argentina, Uruguay, southern Brazil and Paraguay)	Refs [121, 165]
Wetter/Drier	• New Guinea, southern hemisphere mid-latitudes wetter in the north and drier to the south • Hydroclimatic variability over the Amazon Basin	Refs [58, 199]
Drier	• Chile, declining stream flows, consequences for ecosystem health and hydroelectric power	Ref. [235]
More extreme precipitation	• South-eastern South America extreme Summer rainfall • Heavy rain events in Madagascar	Refs [121, 164, 187, 265, 352]

A. Changes in southern hemisphere climate driven by stratospheric ozone depletion	Regional examples	References
Changing ocean and atmospheric circulation		**Chapter 1 and ref.[93]**
Shifting location of wet and dry zones	• Shifts in summer rainfall patterns • Australian summer – increased rainfall on mainland south east coast and decreased rainfall in western Tasmania • Sub-tropical dry zone also shifted towards the South Pole	Refs [30, 132, 150, 206, 265, 287, 306]
Increasing surface wind-stress	• Southern Ocean • Leads to year-round stronger surface ocean warming • Could enhance loss of Antarctic sea ice but see Chapter 1. • Alters mixed layer depth affecting nutrients	Chapter 4 and refs [94, 141, 295]
Temperature		**Chapter 1 and ref.[93]**
Lower temperatures	• Decrease in summer temperatures over East Antarctica, southeast and south-central Australia and inland areas of the tip of southern Africa • Eastern Tropical Pacific cooler	Refs [30, 75]
Warmer temperatures	• Much of Southern Africa warmer • Warmer surface temperature and changed diurnal temperature range in East Africa • Summer extreme temperatures, Australia, South America, Southern Africa	Refs [30, 206]

B. Likely indirect consequences of changes in southern hemisphere climate	Resulting from	References
Changing cloud patterns	Latitudinal shifts in the Hadley and Polar Cells mean that cloud cover has also shifted southward with ozone depletion	Ref.[287] See Chapter 1 for implications for exposure to UV radiation
Fire	Changes in precipitation can alter fire regimes; e.g., central and southern Chile	See Chapter 5 and refs [143, 144, 210]
Dissolved organic matter (DOM)	Changes in precipitation affect run off and quantity of DOM in water bodies	See Chapter 4 for details
Breakdown of litter	Changes in precipitation and temperature influence breakdown rates of litter	See Chapter 5 for details
Air quality	Weather [temperature, wind (transporting pollutants), rain and cloudiness] affects air quality with consequences for health of humans, other animals and plants	See Chapter 6 for details

B. Likely indirect consequences of changes in southern hemisphere climate	Resulting from	References
Weathering of materials	Increased ambient temperature shortens the life of plastics and wood exposed to UV radiation, and their outdoor service lifetimes. Changing moisture also affects these processes	See Chapter 7 for modes of action

C. Drivers of change for terrestrial plants and ecosystems (number of marker on Fig. 3)	Biological effects	Location	References
Decreased water availability			
1	Less precipitation associated with decreasing growth of trees and restricted forest distribution	West New Zealand, South West S. America	Refs [82, 325]
2	East Antarctic drying. Moss beds exhibit changing species composition. Reduced growth, more plant stress and death	Windmill Islands, East Antarctica	Refs [73, 140, 274]
3	Lakes are becoming more saline leading to biodiversity changes		
4	Drying caused more than 80% dieback of cushion plant and moss fellfield communities	Macquarie Island	Ref. [41]
Increased water availability			
5	Less salinity causes changes in lake fauna	Eastern side of the Andes	Ref. [80]
6	More precipitation associated with increasing growth of trees	East New Zealand, Eastern South America	Ref. [325]
7	Expansion of agricultural zones with more precipitation	South East S. America	Refs [121, 124]
8	Moss beds and other biodiversity more productive due to warmer wetter conditions and more land	Antarctic Peninsula	Refs [8, 277, 357]
Increased wind speeds			
9	Risk of increased dust and potential propagule inputs into Antarctica (negative if introduces non-native species)	West Antarctic, Antarctic Peninsula	Refs [68, 116, 219, 223]

2.1.1 Ecosystem responses to fluctuating water availability

Shifting atmospheric circulation cells (Hadley, Ferrel, and Polar cells, see **Fig. 2**) alters regional precipitation across the southern hemisphere, causing some areas to receive more moisture and others to become drier. In Patagonia, declines in tree growth have been linked to reduced water availability (**Fig. 3**; **Table 1B**).[325] In the extreme south of South America extending into Antarctica, lichens are an increasingly-dominant component of the terrestrial biota.[78] Lichens are extremely tolerant of desiccation, but nevertheless the combination of high wind speeds and high irradiance, including increased UV-B radiation due to ozone depletion, have been shown to affect their colonisation on trees in Patagonia.[313] However, lichens grow very slowly,[79] so responses to specific climatic changes can take a long time to detect. Less seasonal precipitation and a reduced diurnal temperature range were the dominant factors driving aridity and limiting the distribution of high-elevation woodlands of *Polylepis tarapacana* (a rose-family species of tree of high conservation value, found in the South American Altiplano). Models predict that by the end of this century almost half of the potential range of this species will be lost due to increased aridity.[82]

Decreased precipitation in this region of South America has led to reduced stream flows in Chile, with adverse effects on aquatic and terrestrial ecosystems as well as the production of hydroelectric power.[235] Since the 1960s, warming and associated drying at mid- and high-latitudes to the west of the Andes have resulted in increased forest fires (measured from fire scars in tree ring records).[143] During the 2016–2017 fire season, more than 500,000 hectares burned in central and southern Chile (between ~29°S and 40°S), driven by a long-lasting drought linked to the positive SAM that was amplified by conditions resulting from the El Niño–Southern Oscillation (ENSO). Given that the positive phase of SAM is predicted to continue, it is likely that the increased frequency of wildfires in southern South America will continue throughout the 21st century.[143]

Several other regions of the southern hemisphere have experienced wetter summers (Chapter 1), leading to increased tree growth in eastern New Zealand[325] and expansion of agriculture in south-eastern South America (**Fig. 3; Table 1B**).[121] The eastern side of the Andes has experienced wetter conditions with associated changes in biodiversity. For example, changes in fauna (ostracods and chironomids) from lake sediments in El Toro Lake (40°S, 70°W) indicate that the lake has become fresher (less salty) as a result of increased precipitation since the middle of the 20th century, associated with the positive phase of SAM.[80]

Increasing extremes of precipitation have also been linked to SAM-related changes. Rainfall patterns in the southern Amazon Basin have been reconstructed from tree rings of *Centrolobium microchaete*[199] and the findings suggest that the fluctuations between drought and extremely wet seasons seen from 1950 to the present day may be unmatched since 1799.

2.2 Changes in surface temperatures because of stratospheric ozone depletion and implications for terrestrial ecosystems

Recent studies[72, 292] suggest that warming of West Antarctica and the Antarctic Peninsula may fall within the range of natural climate variability.[161] This warming had previously been linked to anthropogenic emissions of greenhouse gases and stratospheric ozone depletion.[50, 273] Stratospheric ozone depletion could account for between a quarter and one third of summer and autumn cooling over the rest of the Antarctic continent (see ref.[273]).

However, our confidence in any attribution or projections of climate warming over this region is limited by the large biases inherent in the models used. Depletion of Antarctic stratospheric ozone has possibly offset a substantial portion of the summer warming that would otherwise have occurred (due to increasing greenhouse gases) in eastern Australia, southern Africa and South America (**Fig. 3**).[30] These changes in temperature are likely to have affected (positively and negatively) life cycles of plants and animals, potentially leading to mismatches between plants and their pollinators (see section 7.3). Cooler temperatures over East Antarctica have likely slowed the melting of ice sheets. As stratospheric ozone recovers, the extent of this amelioration may be reduced with potential implications for the climate and populations of these regions as well as further afield.

In western Antarctica, along the Antarctic Peninsula and on nearby islands, increasing temperatures[75] were associated with increased productivity of terrestrial ecosystems (microbial productivity, plant growth rates and carbon accumulation in moss beds) from the 1950s to the turn of the century.[8] There is some evidence that the direction of these changes has reversed since 2000, consistent with recent cooling in this region.[8, 247, 315] However, as noted above, the relative contributions of stratospheric ozone depletion *vs* increasing greenhouse gases to temperature changes is still unresolved because recent studies suggest they are not beyond the range of natural variability (see above and Chapter 1).

In the Windmill Islands of East Antarctica, decreased water availability since the 1960s, linked to decreasing temperatures and increasing wind,[73] has resulted in changes in biodiversity in Antarctic moss beds[274] and lakes,[140] with species composition changing to reflect the newly drier moss beds and more saline lakes. In addition, these East Antarctic plant communities are becoming more stressed as a result of drying, resulting in increasingly moribund moss.[204, 205, 274] This is one of the first studies[274] to document ecosystem-level changes in Antarctic terrestrial plant communities, which are correlated with the SAM and potentially linked to stratospheric ozone depletion and climate change. Further north, widespread (> 80%) dieback of cushion plants *(Azorella macquariensis)* and mosses, on sub-Antarctic, Macquarie Island, was primarily attributed to reduced water availability because of higher wind speeds, more sunshine hours and therefore higher evapotranspiration since the 1970s. The authors estimated that, from 1992 to 2008, these plant communities suffered accumulated water deficit for 17 years.[41] This dieback of Antarctic and sub-Antarctic vegetation is similar to the *"Arctic browning"* observed in the Arctic in response to extreme climate events.[102, 261]

2.2.1 Interannual variability

Two studies have linked interannual variability of springtime Antarctic ozone to summer changes in surface temperature and rainfall in the southern hemisphere.[30, 296] The SAP 2018 report[346] concludes that interannual variability in springtime ozone at both Poles may be important for surface climate, but the extent of this connection is not fully understood.

Stratospheric ozone-driven climate change has widespread and far-reaching effects on terrestrial and marine ecosystems (see Chapter 4) across the southern hemisphere. A better understanding is needed of the relative contributions of stratospheric ozone, greenhouse gases and interannual variability to determine the ecological or biological change attributable to stratospheric ozone depletion *vs* that due to these other climate factors. Nevertheless, we have only included studies in this section where a strong signal of ozone depletion or summer SAM has been associated with an ecological effect.

3 Plant response to UV radiation and interactions with climate change

There is now a basic understanding of UV-sensing and UV-signalling in plants, as well as the consequences for gene-expression, physiology, biochemistry, plant growth, fitness and nutritional quality. Potentially, UV-B radiation can damage plants through effects on DNA, the photosynthetic machinery, and other cellular targets. However, UV-B-induced plant defence responses, including up-regulation of photorepair processes, antioxidant capacity, and UV-screening, are thought to be effective in the prevention of damage to plants by UV-B radiation under most natural conditions. Nevertheless, effective prevention and repair do not imply that UV radiation has no effect on plants. Acclimation to UV radiation and climate change factors can modify plant growth and development, which, in turn, has consequences for ecosystem functioning (section 6), nutritional quality, and food security (section 5). Thus, understanding plant response to UV radiation and some of the interactive effects of climate, is of fundamental importance for evaluating effects of UV-B radiation on terrestrial ecosystems.

3.1 Limitations to current studies investigating interactive effects

Much of our understanding of plant responses to UV radiation began with single-factor experiments in laboratories, greenhouses, and controlled environment chambers that did not account for interactive effects from multiple climatic variables. Overall there is evidence that conditions in artificial environments may unrealistically accentuate the negative effects of UV-B radiation on plant growth. For instance, such studies are often conducted in growth chambers or greenhouses where lamps are used as the principle source of UV-B radiation and the ratio of UV-B radiation to photosynthetically active radiation (PAR, 400–700 nm) is far above that generally found in field conditions. We illustrate these limitations for some recent controlled-environment studies (**Fig. 4**). Note that only 16 of the 49 studies surveyed provided enough UV and PAR data to be represented as data points in the figure.

It is important to use the knowledge from these studies to design experiments for testing the results at more expansive scales of space and time. Laboratory results may be scaled up by progressively moving to more realistic conditions in controlled environments and then to field experiments (e.g., ref.[111]). Another scaling approach is to design experiments moving from our common organism-centered methodology to a community or ecosystem perspective, where interactions, feedbacks, and their relative magnitudes under realistic conditions are examined.[108] Some recent studies have investigated the effects of UV-B radiation in combination with other variables related to climate change, such as drought, temperature, carbon dioxide, and tropospheric ozone (e.g., refs [209, 216, 342]). For this assessment, we evaluated the experimental studies and methodological protocols,[10] resulting in the exclusion of some studies in our summary findings.

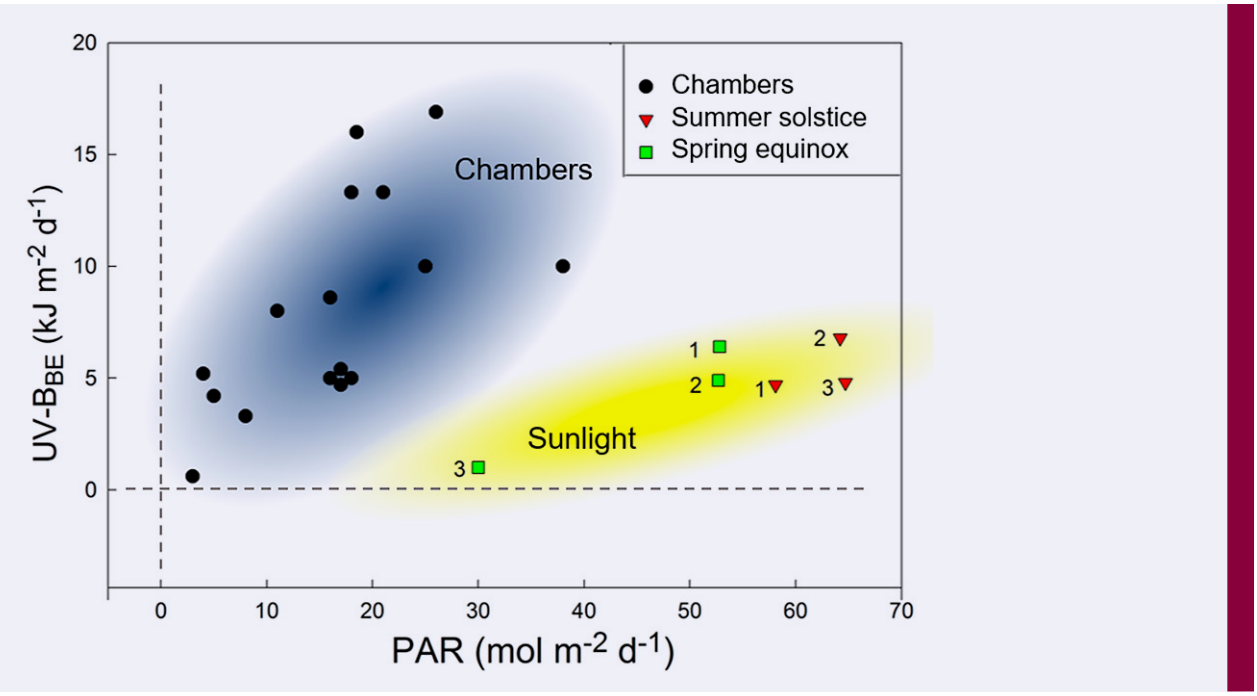

Fig. 4 **Studies conducted in growth chambers (blue) are still using unrealistic ratios of photosynthetically active radiation (PAR, 400–700 nm) to biologically effective UV-B radiation (UV-BBE; data were reported using the generalized plant action spectrum of Caldwell *et al.*[60] (more commonly used in these studies than the action spectrum of Flint *et al.*[113]) compared with natural sunlight (yellow). Growth chamber experiments are represented by black circles within the blue shading. Solar irradiances within the yellow shading represent the summer solstice (red triangles) and spring equinox (green squares). Ambient PAR is from[270] and ambient UV-B_{BE} was computed with the TUV calculator: http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV. Latitudinal locations are indicated by numerals: 1. Equator (0°), 2. Tropic of Cancer (23°N), and 3. 55°N. A total of 49 peer-reviewed papers on growth chamber studies from the years 2011–2017 were surveyed; 16 are represented as data points in this figure and 33 could not be represented, because they either lacked radiation data or it was not measured in a manner comparable to the other studies.**

3.2 The UV-B photoreceptor and signalling pathways

The existence and nature of a specific UV-B photoreceptor in plants, the protein, UVR8, initially came to light in 2011.[271] Since this discovery, a basic understanding of UV-sensing, signalling and function has emerged that has improved our knowledge of the molecular mechanisms underlying UV defence and acclimation in plants.[159, 271, 356]

UVR8-mediated perception of UV-B radiation contributes to up-regulation of the expression of genes that encode components of the phenylpropanoid biosynthesis pathway, photorepair of DNA damage, and enhanced antioxidant capacity.[159] Penetration of UV-B radiation into leaves depends on the concentration of flavonoids and other phenolics in the epidermis, as well as plant anatomical and morphological characteristics that vary among species. Most of the UV-B radiation is strongly attenuated as it passes through the epidermis, although it has been measured in some herbaceous plant species in deeper-lying tissues (mesophyll layers), with 18–41% epidermal transmittance.[51, 86] Given that the UVR8 protein has been detected in most plant tissues investigated, including roots, it is currently difficult to pinpoint in which

plant tissues perception of UV-B radiation takes place in plants growing in sunlight. Tissue-specific analysis of UVR8 activity has revealed that the UV-B-induced UVR8 signalling pathway in epidermal and mesophyll cells is involved in hypocotyl elongation, while UVR8 expression in the epidermis contributes to cotyledon expansion.[42] Thus, the UV-B-induced response appears to be partly mediated by tissue-autonomous signalling, although inter-tissue signalling may also be involved.[42] The role of UVR8 is not simply limited to protection from UV-B radiation. There is now strong evidence that UVR8-mediated signalling extends to processes such as stomatal function, de-etiolation (greening response of plants), entrainment (alignment with) the circadian clock, phototropism, and defence against pathogens.[356] These findings, mainly on the model plant, *Arabidopsis thaliana* (a type of cress), provide a frame of reference for the study of the multifaceted role of UV-B perception through photoreceptor(s) in the regulation of plant growth and development in the much more complex natural environment. This frame of reference can also be used for other plant species that are likely to follow a variety of strategies to acclimate and adapt to their habitats.

While much attention has been given to elucidating UVR8-mediated processes, UVR8 is not the only UV-B sensing mechanism in plants. There are also UVR8-independent signalling pathways,[185] for example, arising from oxidative stress and via UV-B-mediated DNA damage,[43] including generation of cyclobutane pyrimidine dimers (CPD, one of the main types of DNA damage). However, CPD photolyase, which repairs the damage, is predominantly regulated in a UVR8-dependent manner in plants exposed to UV-B radiation. There is evidence that the UVR8-mediated signalling pathway regulates the scavenging capacity of reactive oxygen species (ROS),[138] and the production of nitric oxide in response to UV-B-induced stress.[312] These latter molecules may themselves play a role in signalling.[312]

Thus, plant response to UV-B radiation likely involves multiple UV-signalling pathways. Moreover, components of these UV-mediated signalling pathways interact with other stress-induced signalling pathways, such as those activated by other wavelengths of light, exposure to drought, extreme temperatures, and other factors associated with climate change.

3.3 UV-B-mediated signalling, crosstalk and cross-tolerance

There is still a lack of information and understanding concerning the effects of UV-B radiation in a complex environment where plants are simultaneously or sequentially exposed to multiple environmental factors that can modify plant growth and development.

In principle, the simultaneous application of treatments involving changes in two environmental factors can lead to additive, synergistic, antagonistic, or no effect. It is particularly relevant from an agronomic perspective that acclimation responses induced by changes in one environmental factor can confer cross-tolerance (including priming responses) or cross-sensitivity to another factor. Exchange of information between distinct plant-signalling pathways can broaden the spectrum of responses to one environmental factor. For example, high levels of PAR and UV-B radiation generally increase the accumulation of flavonoids, with synergistic effects occurring in some cases when plants are exposed to a combination of both variables.[35, 234] Such increases of protective pigments with antioxidant activity potentially enhance the tolerance of a plant to a variety of unfavourable conditions.

Cross-talk also occurs when UV-B-mediated signalling cascades interact with signalling pathways induced by biotic variables, e.g., bacteria. This cross-talk can sometimes lead to a

shift in other plant defences at the expense of the UV-induction of protective mechanisms, such as the accumulation of flavonoids.[15] In this case, the UV-B-induced genes of the flavonoid pathway are suppressed by the bacterial elicitor, flg22 (a peptide), which, in turn, drives the immune response against the bacterium[361] by stimulating pathogen-protective compounds called phytoalexins. In other cases, UV-B radiation can increase plant resistance against pathogens and pests, by increasing the accumulation of metabolites involved in plant defence against multiple stress factors (reviewed in ref.[24]). Other examples of cross-talk where UV-B radiation is implicated in plant stress responses include changes in some plant hormones, such as auxin, cytokinin, gibberellic acid, brassinosteroids, and jasmonic acid.[109, 186, 281] UV-cross-talk involving the hormone abscisic acid can result in increased plant tolerance to water stress, extreme temperatures, or salinity. Some of these aspects are evaluated in the next section.

The interactions between UV-signalling and other signalling pathways imply that subtle molecular effects of UV-B radiation may potentially extend to many aspects of growth and development, with implications for ecosystems including agricultural systems under conditions of current and future climate change.

3.4 Plant and ecosystem response to potential interactive effects of UV-B radiation and climate change factors

Exposure to changing environmental conditions can directly affect plant growth and may also drive changes in phenology (section 7.3) and shifts in the distribution ranges of species (section 7.1). Here we will specifically explore interactions between UV-B radiation and certain key abiotic climate variables. In comparison to studies on interactive effects of UV-B radiation and drought and/or temperature, far less is known about interactive effects of UV-B radiation and elevated CO_2 on plants.

3.4.1 UV radiation and drought

The potential for plant responses to UV radiation and drought to reinforce each other has been the subject of research because seasonal droughts are usually coincident with, or follow, periods of prolonged sunny weather, implying high exposure to UV radiation. An example of such synergies comes from an experiment with seedlings of silver birch (*Betula pendula* L.) subjected to treatments combining solar UV-B radiation and water stress outdoors in southern Finland. In this investigation, leaf and whole plant water potential responded to the combination of ambient UV-B radiation, conferring resistance to drought, which was visible through reduced wilting and lower mortality beyond that of UV-B radiation or water stress alone.[275] Plant response to the combinations of UV-B radiation and drought should be considered when selecting agricultural crops because of potential consequences for crop quality.[215]

Additional research provides evidence for synergies in response to drought and UV-B radiation.[134, 172] However, both the mechanisms and outcome of response to combinations of water stress and UV-B radiation are often inconsistent. To some extent, the seemingly contradictory results reflect differences among studies in the timing and levels of drought and UV-B radiation applied to the plants. Sequential exposure to two environmental variables can allow the first to elicit a response that primes the plant for the second, resulting in cross-protection. In contrast, simultaneous exposure may weaken plant defences.[31] In this context,

it should be noted that few, if any existing studies have adequately reproduced natural combinations of exposure to UV-B radiation and drought as well as their relative timing, and therefore results from these studies need to be carefully evaluated for their relevance (see **Fig. 4**).

Reduced cloudiness is expected to lead to increases in UV-B radiation and future seasonal droughts in Mediterranean ecosystems.[21, 280] A study where solar UV radiation was filtered in a Mediterranean ecosystem under normal and reduced rainfall, showed plants to be tolerant of UV-B radiation independently of the rainfall regime and seasonal climatic conditions. In this case, the species tested were evergreen Mediterranean shrubs with tough thick leaves high in phenolics.[321] Thus, life history, together with exposure protocols, choice of species, and dose-dependency will all determine the outcome of the interactive effects of drought and UV-B radiation.

Perhaps the most important complication in attempting to understand the interactive effects of drought and UV-B radiation, is that both variables alone induce complex responses, and any simultaneous exposure to both variables will result in an amplification of that complexity. Cross-protection is multifaceted and likely to involve decreases in leaf area and possibly stomatal gas exchange, increases in leaf and cuticle thickness, as well as enhanced concentrations of antioxidants, flavonoids and potentially a range of other secondary metabolites such as proline and volatile terpenes.[7] Osmotic stress-induced upregulation of the UVR8 transcript and protein levels might also contribute to interactive effects of drought and UV-B radiation.[105] This complexity can also be observed in a study where drought, in the presence of a background of UV radiation, increased canopy temperature in a grassland ecosystem, resulting in decreased accumulation of above-ground biomass.[244] Thus, interactive effects of drought and UV-B radiation need to be considered in the context of prevailing and future conditions, particularly warming temperatures.

3.4.2 UV radiation and temperature

On balance, rising average air temperatures associated with climate change are expected to affect the growth and survival of many plant species and animals, and perturb many ecosystem processes. In addition to changes in average temperatures, extremes in temperature have increased in frequency and magnitude,[286] which can have severe local and regional consequences. Changes in seasonal weather patterns and sky conditions are bringing periods of high temperatures, which are often accompanied by high solar radiation including UV-B radiation to many regions. However, extreme cold temperatures can also be accompanied by high UV-B radiation, particularly at high elevations and latitudes in springtime where UV-B radiation reflected by the snowpack[259] often supplements the irradiance received by organisms exposed to the sun.[168] The combinations of UV-B radiation and temperature can affect acclimation processes in plants (see below), which are important in terms of understanding the response of ecosystems to climate change, how future agroecosystems will be managed, as well as how vegetation itself affects air quality and climate (see Chapter 6).

Exposure to high UV-B radiation and elevated temperatures elicits a variety of chemical responses in plants. For example, UV-B radiation can induce production of volatile hydrocarbons, such as the isoprenes,[194] and this has been associated with heat tolerance mediated by membrane stabilisation. Typically, emissions of isoprene occur in woody plants, contributing to air pollution and global carbon. Global annual emissions of isoprene are

estimated to be equivalent to 300 Tg carbon yr^{-1} (= 300×10^{12} g C yr^{-1}) with changes depending on climate change and land-use.[127] Isoprenes, as well as other plant-produced biogenic volatile organic compounds such as monoterpenes, have an important effect on atmospheric composition, and ultimately climate. Exposure to elevated temperature combined with UV-B radiation can cause more isoprenes to be emitted than under elevated temperature alone, as was found for European aspen.[203] UV-induced isoprene production is synergistically enhanced in response to higher temperatures, and this has significant implications for both plant thermotolerance and plant-herbivore interactions.[104]

An outdoor field experiment in Finland found that supplemental UV-B radiation enhanced accumulation of condensed tannins in aspen, but this increase was negated by a temperature treatment of 2°C above ambient in the spring and summer.[266] This process may directly impinge on herbivory, given that tannins act as defence compounds that inhibit digestion (also see section 6). In willow, the same combination of UV-B radiation and temperature produced a similar pattern of effects on the accumulation of phenolic compounds.[245]

It is well known that the total content and composition of flavonoid compounds in plant leaves can be modified by a number of environmental factors including UV radiation, and high and low temperatures.[76, 238, 249, 260, 349] For example, kale (*Brassica oleracea* var. *sabellica*) exposed to a low temperature of 5°C accumulates almost twice as much of the polyphenol, kaempferol-3-O-sophoroside-7-O-glucoside, as plants at 15°C. Such stimulatory effects may also completely mask UV-B-induced accumulation of flavonoids, as was seen in an outdoor study where plants under low temperatures accumulated high concentrations of UV-screening pigments, and this response was unaffected by the UV-exposure regime.[76] However, the profile (or composition) of the polyphenols is also modified, whereby kale plants at 15°C accumulate ca 25% more kaempferol-3-O-caffeoyl-sophoroside-7-O-glucoside but 30% less kaempferol-3-O-sophoroside-7-O-glucoside.[238] At present, the function of these changes in phenolic profiles are not clear, although some of the compositional changes result in compounds with higher antioxidant activity. Since flavonoids are considered desirable by the food and nutrition industries (see also sections 5.2 and 5.3), an understanding is needed of changing phenolic profiles under different environmental conditions.

4 Perception of and response to UV radiation in animals

Ulraviolet-B radiation has the potential to damage tissues in animals, but many animals, like humans (Chapter 2), have mechanisms that protect against the potentially deleterious effects of UV-B radiation. Nonetheless, there are reported cases of UV-induced injury in animals (see section 4.1; and ref.[50]). Apart from UV damage, many animals perceive UV radiation and can use these cues to lessen exposure to intense UV radiation. Also, some animals use UV radiation as a source of information for mate selection, foraging, predator avoidance, and other behaviours. Traditionally, an anthropocentric or human-centric perspective has resulted in a narrow definition of "visible light," appropriate only for human vision. However, it has long been known that many species have vision that encompasses different wavelengths of the spectrum, sometimes including the UV region. Animals known to have UV vision include species of insects, amphibians, reptiles, birds and mammals.[81] While advances have been made in understanding the mechanism of UV vision in animals, it is unclear how changes in the UV environment, as a consequence of changes in stratospheric ozone and climate change, might alter the UV sensory responses of these organisms (see section 4.2).

4.1 UV radiation damage to animals

Ultraviolet-B radiation is known to be potentially deleterious to a wide variety of terrestrial animals. Under controlled conditions, it has been shown that UV-A and UV-B radiation can damage the skin and eyes of various amphibian species (e.g., newts, frogs, bullfrogs, treefrogs), with the potential to negatively affect their foraging ability and fitness (reviewed by refs[29, 47]). For example, in South America, there are indications that land-use and climate change may lead to increased exposure to UV radiation in the habitats of frog species, e.g., *Hypsiboas curupi* and *Hypsiboas pulchellus*.[193, 198, 254] However, while UV radiation may impair vision and cause DNA damage to frogs, it is not considered at present to be among the most important environmental factors contributing to the reduced fitness and abundance of several frog species in this region.[66]

4.2 UV vision in animals and ecological implications in changing environments

The eyes of insects and mites have specific rhodopsin photoreceptors that perceive UV radiation,[225] which may be important in avoiding excessive UV radiation.[222] In other insects, such as damselflies, UV-reflecting wings appear to play a direct role in mate recognition by creating visual signals of sex and age.[125]

Some birds have UV-A vision and photoreceptor UVS-cones (sensitive to wavelengths longer than 355 nm), which may assist in foraging and mate choice.[81] For instance, woodpeckers use visual cues in the UV-A region to forage on decaying wood, which differs in UV-absorption according to the extent of its fungal colonisation. Changes in the amount of UV radiation in the environment (e.g., due to changing weather patterns or forest cover) may affect visibility of these fungi and hence alter the behaviour of woodpeckers foraging for them. Changes in mutualisms of this sort have broad consequences for ecosystem function.[246] In other birds, UV-absorbing melanin in their feathers has been linked with sexual selection, UV-protection and thermoregulation, and UV protection over wide geographic gradients.[118] Many species of bird display strong sexual differentiation (dichromatism), creating specific patterns through both accumulation of melanin and UV-reflectance of feathers.[87] UV patterning,[233] including UV-absorbance and reflectance, are not limited to feathers and their putative role in mate selection, but are also used in a much broader range of visual recognition processes. For example, UV-reflection of bird eggs attracts aerial predators.[233, 354] Conversely, UV-absorbing melanin in egg shells may protect eggs from UV-B radiation directly and reduce their visibility to predators, although the dark pigmented colour may cause overheating in some environments. Across a variety of species, including a palmate newt *(Lissotriton helveticus),* the expression of SWS1 opsin, a UV-photoreceptor in the eyes of animals, is UV-dependent;[191, 214] furthermore, plasticity in expression of the photoreceptor depends on the habitat of origin of the population. This suggests that changes in the amount of UV radiation in the environment during the development of these newts could affect visual sensitivity in the UV region.[114, 284]

The role of UV-B radiation has been relatively well-studied in the case of lizards. Lizards kept in captivity are routinely exposed to low background levels of UV-B radiation to enhance vitamin D synthesis and their overall health.[97] UV-reflectance of lateral blue spots in male lizards has a clear role in male-male interactions, including the processes of mutual

assessment.[213] If two males have an equal signal from their UV-reflecting throat patch, their behaviour towards each other is more aggressive.[212]

At present, evidence for an ecological role of UV vision in animals is steadily increasing, but detailed information of the functional role of UV-absorbing or reflecting tissues often remains a matter of speculation. There is also a lack of information on the dose-response of UV-visual recognition processes. Thus, it is not known how changes in stratospheric ozone and climate change-driven alterations in exposures to UV radiation will influence visual cues in animals or whether altitudinal or latitudinal gradients in UV radiation might affect migration or range shifts in these animals. Nevertheless, understanding of UV vision in animals is of direct relevance in the context of food security and specifically plant-pest and plant-pollinator interactions.

5 Food security and agricultural ecosystems

At mid-latitudes and the tropics, there are indications of recovery of ozone in the upper stratosphere. However, the total ozone column, which is the metric of greatest relevance for terrestrial ecosystems, has not yet started to recover. Because of increasing concentrations of greenhouse gases, the total ozone column over mid-latitudes will be larger by the second half of the 21st century compared to the time prior to the release of the ozone depleting substances into the atmosphere. Changes in total ozone over the tropics will be relatively small and will depend on emission scenarios and climate change-related phenomena (Chapter 1 and ref.[20]) Nevertheless, the relatively high levels of UV radiation that occur in the tropics and at high elevations, together with ozone-independent, location-specific factors such as decreasing concentrations of aerosols, less cloud cover, and changes in land-use (Chapter 1), mean that crops may still be subject to significant changes in exposure to UV radiation. Some areas will also receive less UV radiation where pollution levels continue to be high, including increasing frequencies of smoke from forest fires (Chapter 4). These levels of complexity can affect agroecosystems with respect to growth, development and survival. It is in this context that crop plant and agricultural responses to UV radiation and climate change will be assessed here. Particular attention is given to defence mechanisms of plants, implications of genotype, and changes in crop quality mediated through changes in their biochemistry.

5.1 Linking UV radiation and climate effects to food security

The interactive effects of UV radiation, climate change, and changes in land-use and management practices are likely to have consequences for agriculture and food security. For example, these factors can modify yield and crop quality, pest and disease resistance, and overall vulnerability or adaptation to the environmental changes (**Fig. 5**). From the human intervention perspective, clearing of land for increased agricultural production to cope with growing populations, leads not only to increased exposure of agroecosystems to UV radiation, but also to poorer quality of soils and soil erosion. In areas receiving increased UV radiation, plants may more readily express acclimative mechanisms against disease, herbivores, and other environmental stresses. Farmers and growers are also becoming increasingly interested in the advantage of UV-induced stimulation of desirable secondary metabolites, such as the polyphenolics, in order to achieve improved crop response to stress conditions, including drought, pests and diseases.[1, 100, 142, 146, 334, 335]

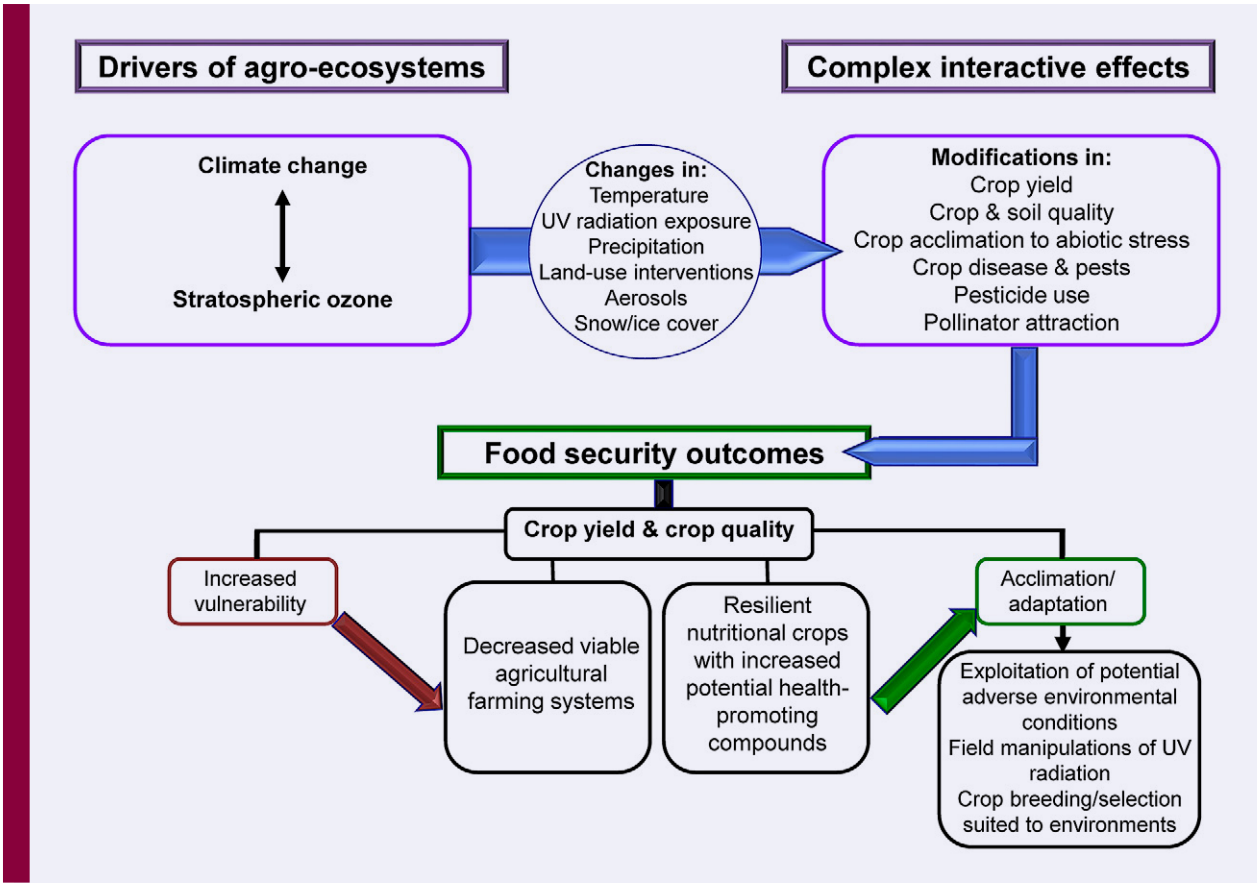

Fig. 5 **Examples of current and evolving drivers of change on food security, showing the effects of linkages between changes in stratospheric ozone and climate.**

5.2 Effect of genotype and environment on crop yield and quality

The degree of acclimation of plants to stress conditions is often dependent on cultivar or genotype,[201, 314, 349] as well as location and growth conditions.[95, 349–351] Environmental conditions and genotype have been shown to be key factors that determine plant response and yield, and are indicative of the general phenotypic plasticity of plants (changes in morphological, physiological and metabolic attributes). The roles of both the environment and genotype are especially important when assessing current and future plant acclimation to stressful environments, including locations exposed to high levels of UV-B radiation, low rainfall, and extremes of temperature (e.g., Andean Altiplano and Tibetan Plateaux). Thus, research investigating the 'environment x genotype' response of crop plants is important for selection of genotypes suitable to particular environments and levels of UV-B radiation. The composition, concentration and antioxidant activity of polyphenolics change according to exposure of plants to elevated UV-B radiation and vary strongly with plant genotype.[250, 349] Because of the potential benefits of antioxidants (conferring free radical scavenging capability) and other plant components, the selection of responsive genotypes or cultivars can be used to improve the nutritional status of a crop.[242] These benefits may include the potential for reducing the risk of health-related diseases such as cardiovascular disease and Type 2 diabetes.[268, 316, 341]

5.3 Importance of secondary metabolites in agro-ecosystems

Ultraviolet-B radiation regulates the accumulation of numerous secondary metabolites, including flavonoids and other compounds derived from the phenylpropanoid pathway. These metabolites are important for plant growth and development, as antioxidants, UV-screening pigments, herbivore and pathogen deterrents, as well as serving as pollinator attractants and improving nutritional quality,[310, 328] flavour, visual appeal, and desirability of many foods (see refs.[50, 65, 163, 218, 288, 298, 302, 335] and references therein). However, exposure to UV-B radiation may cause both desirable and less desirable changes in nutritive properties. For example, UV-B radiation can decrease protein content in some crops or increase essential fatty acids not synthesised by humans and other animals (i.e., polyunsaturated linoleic and linolenic acids), while decreasing other beneficial fatty acids, such as the monounsaturated oleic acid, as was found in a study on soybean seeds.[269]

The UV-B-induced regulation of phenolic compounds can occur under low levels of UV-B radiation in many plant species, including in a range of economically important crops in which these metabolites contribute to food quality and/or value. For instance, UV-B radiation mediates increased accumulation of the potentially nutritionally-valuable flavonoid compounds, quercetin and kaempferol, in skins of grapes.[195] The phenolic composition of grape-skins can also change along latitudinal gradients. This was shown in a study where these flavonoid compounds were favoured in the south compared with the north (from 36.7°N Jerez, Spain to 50°N Geisenheim, Germany), a change which positively correlated with overall solar radiation across multiple European sites.[88] This finding suggests that field manipulation of the exposure of grapes to UV-B radiation and other fruit crops could be exploited to enhance desirable characteristics. Such field manipulations are already in development.[126, 133, 255, 335]

Although UV-B radiation can affect food quality, this does not only involve phenolics, but a much broader range of metabolite classes including UV-regulated terpenoids, aromatic esters and others.[297] In peaches exposed to UV-B radiation, levels of the flavour-related monoterpene, linalool, decrease, while concentrations of sesquiterpene (E,E)-α-farnesene increase.[194] Volatile isoprenes have also been associated with thermotolerance (see section 3.4). Specific glucosinolate compounds may also accumulate in plants exposed to UV-B radiation,[130] and may lead to the production of certain defence compounds against herbivory, creating another link with observations of reduced herbivory in plants exposed to UV-B radiation (see section 6.2), although the degree of resistance to herbivory under UV-B radiation may also be dependent on the type of herbivore (see ref.[104]; and section 5.4).

Decreases in UV-B radiation in southern South America and Australasia as the stratospheric ozone layer recovers (Chapter 1), may have negative effects for plants and agricultural crops in some cases. For example, as noted above, since UV radiation generally enhances production of plant secondary metabolites that deter many plant herbivores[104], a decreased induction of these polyphenolics may result in increased herbivory and plant disease. It follows that from an environmental and food safety perspective, reduced cross-protection against herbivores, resulting from decreased UV-induced accumulation of phenolic compounds in crop plants under projected lower future UV-B radiation exposures, may result in increased pesticide use.[27] There is also evidence that UV radiation can promote the breakdown of many pesticides (e.g., fenitrothion[340], triazophos[180, 267]).

5.4 Potential effect of UV radiation on the visibility of crops to insect pests and pollinators

As well as being herbivores, insect pests are the main carriers of plant viruses, which are a major cause of plant disease and restrict yields through decreased plant vigour.[9] In agricultural and horticultural environments, reductions in UV radiation, whether through climate change (e.g., cloudiness, aerosols, forest fires) or deliberate intervention (e.g., the use of UV-attenuating screens, plastic films or nets), can reduce visibility of crops for some insect pests. However, certain pests, such as whitefly, aphids, and thrips may be more damaging to crops in environments with UV radiation compared with environments where UV radiation has been attenuated or reflected,[9, 179] although exceptions have been reported.[26, 176] On the other hand, some beneficial insects such as pollinators, are more effective in environments containing UV radiation, allowing them to use floral cues such as UV-absorbing/reflecting nectar guides (reviewed in ref.[196]). The floral patterns produced by nectar guides can be species-specific as found in the genus *Potentilla* where flowers of species from different regions of its distribution appear similar in the visible spectrum but differ in their UV nectar guides, presumably as an adaptation to attract different pollinators (**Fig. 6**).

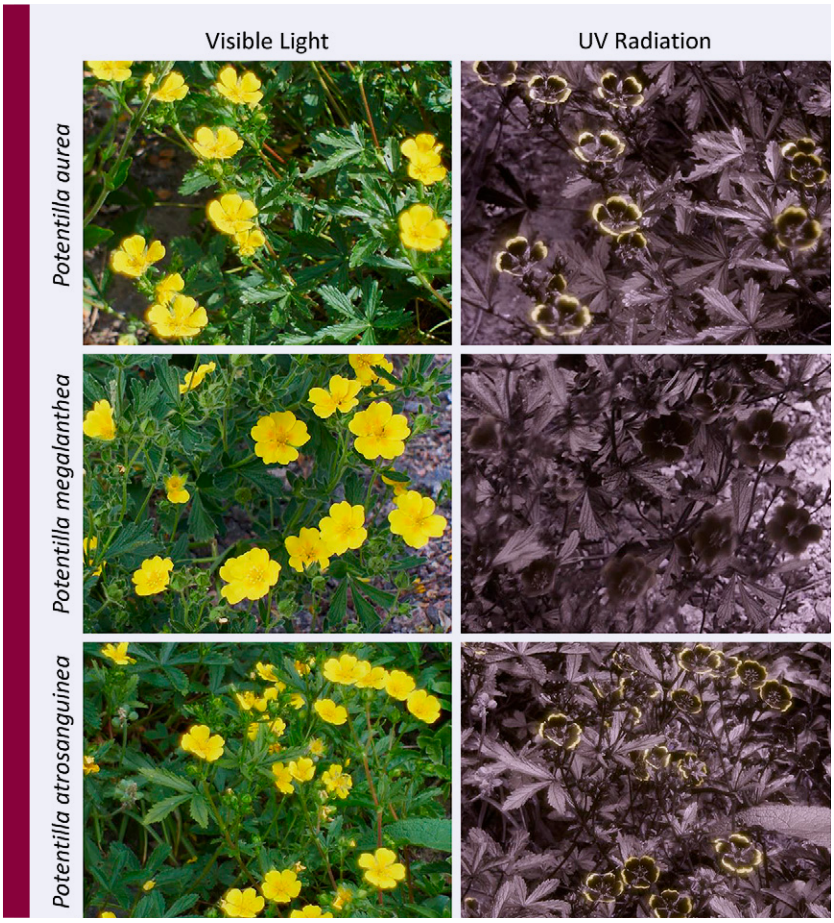

Fig. 6 **The three *Potentilla* species with different origins growing together in Helsinki Finland: *Potentilla atrosanguinea var. argyrophylla* (Himalayan cinquefoil) originates at high elevations; *Potentilla megalanthea* is from Japan; and *Potentilla aurea* is European. While looking similar in the visible spectrum their flowers have very different UV-absorbing and reflecting nectar guides that are visible to insect pollinators. UV photographs were taken with a filter blocking visible radiation but transmitting in the UV-A as far as 325 nm. Photographs by T.M. Robson and P.J. Aphalo.**

These effects of UV radiation on insects have implications for crop yields and the use of agro-chemicals to control pests. However, in controlled environ-ments, growers must balance the benefits of UV radiation for plants providing higher food quality[178, 211] against any potential

costs in terms of the visibility of the plants to pests such as fruit flies *(Drosophila suzukii*[180]*)* thrips and aphids.[1, 148]

Thus, the interplay of changing levels of UV-B radiation and increased frequency of extreme weather events is likely to add to the current and projected vulnerability of agriculture with consequences for food security (**Fig. 5**). The key climate drivers together with UV-B radiation that modify plant development and yield are usually temperature and water availability.[241, 289, 290] Consequently, the capacity of plant acclimative mechanisms to adjust to the rapidly changing conditions will become increasingly important.

6 Ecosystem functioning

Terrestrial ecosystems can be modified in several ways by the interactive effects of ozone depletion, UV radiation and climate change. Below, we consider recent findings that address the impacts of these interactions between plants (plant-plant), plant-herbivore, pest-pathogen, and litter decomposition. Some of these processes, particularly litter decomposition, are important in biogeochemical cycles. The consequences of alterations in these ecosystem processes for nutrient cycling and climate change are addressed more fully in Chapter 5.

6.1 Plant-plant interactions

Plants interact with one another in positive (facilitation) and negative (competition) ways and these interactions can ultimately change the composition of plant communities and their development following disturbance (succession). Competition between crops and weeds is also an important process affecting agricultural productivity and can require considerable labour and economic investment in weed control. Past studies have shown that enhanced UV-B radiation can shift the balance of competition between crop and weed species, and that these changes are linked to differential effects of UV-B radiation on plant morphology, which then alters competition for light within plant canopies (reviewed in ref.[37]). Similarly, exposure to ambient UV-B radiation has been shown to change species composition in alpine plant communities, and these changes were also associated with differential effects of UV-B radiation on plant height and leaf area.[355] Modelling studies confirm that these differential effects of UV-B radiation on plant growth and morphology can lead to shifts in competitive relationships among species.[301] At least some modifications to shoot morphology are likely mediated by the UV-B photoreceptor, UVR8.[159, 271] Plants appear to use UVR8, along with other photoreceptor proteins (e.g., phytochromes), to sense changes in the light environment caused by the proximity of other plants.[129, 220] Conditions of low light (shade) inactivate UVR8, which then results in plant resources being redirected from defence to rapid growth.[220] However, while this strategy helps the plant to compete for light with its neighbours, it also makes it more vulnerable to the attack of pathogens and pests (reviewed in refs[24, 28]; see section 6.2 below).

6.2 Herbivory and plant-pathogen interactions

Plant responses to UV-B radiation have consequences for organisms at various trophic levels or positions along the ecological food chain from producer to consumer. Solar UV-B radiation-induced reductions in herbivory have been well-documented in the field, and when this occurs, may be proportionally much larger than the effects of UV-B radiation on inhibiting plant growth (reviewed in ref.[26]). However, there are also instances where herbivory increases

with UV-B radiation (see section 5.4). Herbivorous insects can perceive solar UV-B radiation,[221] although many of the inhibitory effects of UV-B radiation on insect herbivory and pathogens are thought to be indirect (i.e., mediated by changes in host-plant chemistry; reviewed in ref.[24]). More limited evidence indicates that solar UV-B radiation can reduce infection by some plant pathogens. This increased pathogen resistance was observed in experiments where plants were pretreated with different amounts of UV-B radiation before inoculation with a pathogen.[91]

Shade-intolerant plants often down-regulate or decrease their defences against pathogens and pests in those leaves that are exposed to shade or shade signals (such as a low red to far-red ratio, R:FR),[68, 152, 183, 231] presumably allowing for resources to be redirected into growth responses to avoid shade. According to this interpretation, plants growing in patchy canopies use solar UV-B radiation as a "gap" signal to adaptively regulate their growth and defence phenotypes. The interplay between shade signals (such as low R:FR perceived by phytochromes) and gap signals (such as high levels of UV-B radiation) may optimise the allocation of resources between growth and defence (see ref.[90] and reviews [24, 220]).

Some of the changes in plant chemistry elicited by natural levels of solar UV-B radiation involve compounds known to be important for plant interactions with other organisms (reviewed in refs[104, 343]). Known defence-related compounds regulated by UV-B radiation include phenylpropanoid compounds,[153] isoflavonoids,[98, 358] conjugated polyamines,[90] cuticular waxes,[177] proteinase inhibitors,[154, 300] and jasmonates,[99] among others. These effects of solar UV-B radiation on defensive chemistry can be considered as specific, presumably mediated by specific UV-B photoreceptors. However, the role of UVR8 in mediating effects of UV-B radiation on secondary compounds has so far been demonstrated only for flavonoids and other soluble phenolic compounds.[91, 230]

In spite of the effects of UV-B radiation on plant defence against several herbivores and certain pathogens, the connections between UV-B radiation and the key hormonal pathways that regulate plant defence (i.e., the salicylic acid (SA) and jasmonic acid (JA) pathways), require further research. Early reports of effects of UV radiation on SA and expression of marker genes for SA should be interpreted cautiously, as many of those experiments used doses or wavelengths of UV radiation not present in the terrestrial environment (such as UV-C, < 280 nm), or unbalanced UV-B radiation treatments (high UV-B radiation delivered against low PAR; see **Fig. 4**). Similar limitations apply to early studies of effects of UV radiation on JA activity (reviewed in ref.[24]).

Some well-characterised effects of UV-B radiation on plant defence come from experiments that tested plant resistance to herbivorous insects, and necrotrophic pathogens (pathogens that kill their host cells). This has led to follow-up work focusing on interactions with JA-signalling. A few studies have shown that genetic perturbations impairing synthesis of JA can effectively cancel out some anti-herbivore effects of solar UV-B radiation, leading to the suggestion that JA-signalling is required for those effects of solar UV-B radiation that increase plant resistance to herbivory.[64, 90, 263] However, UV-B radiation can also affect plant defence against herbivores and pathogens via mechanisms that are not mediated by JA.[91] The positive effects of UV-B radiation on JA-signalling have been attributed to increased biosynthesis of JA[99] or sensitivity,[90] but the molecular mechanisms linking perception of UV-B radiation and JA- signalling remain to be elucidated.

6.3 Decomposition of litter

The decomposition of dead plant material (i.e., litter) drives the rate at which nutrients are recycled and is a strong determinant of carbon storage and soil fertility in terrestrial ecosystems. In general, the overall rate of decomposition is dependent on the temperature and moisture availability, which affects the activity of decomposing micro-organisms (bacteria and fungi), as well as the type of plant litter inputs (e.g., leaf *vs* woody tissue; evergreen *vs* deciduous leaves). Substantial evidence now indicates that solar radiation (UV and short wavelength visible radiation) can also drive litter decomposition via several mechanisms, with the net effect of these processes either accelerating or retarding decomposition, depending on quality of the litter and environmental conditions. Climate change will likely alter the importance of UV radiation in decomposition and in regulating cycling of carbon in a number of terrestrial ecosystems.

Solar radiation in the UV and short-wavelength visible regions (blue and green light) can directly break down the biochemical components of plant tissue, including relatively stable compounds, such as lignin, which absorb UV radiation, through a process called photochemical mineralisation (**Fig. 7**; refs [25, 38, 166]). These light-driven modifications in litter chemistry can, in

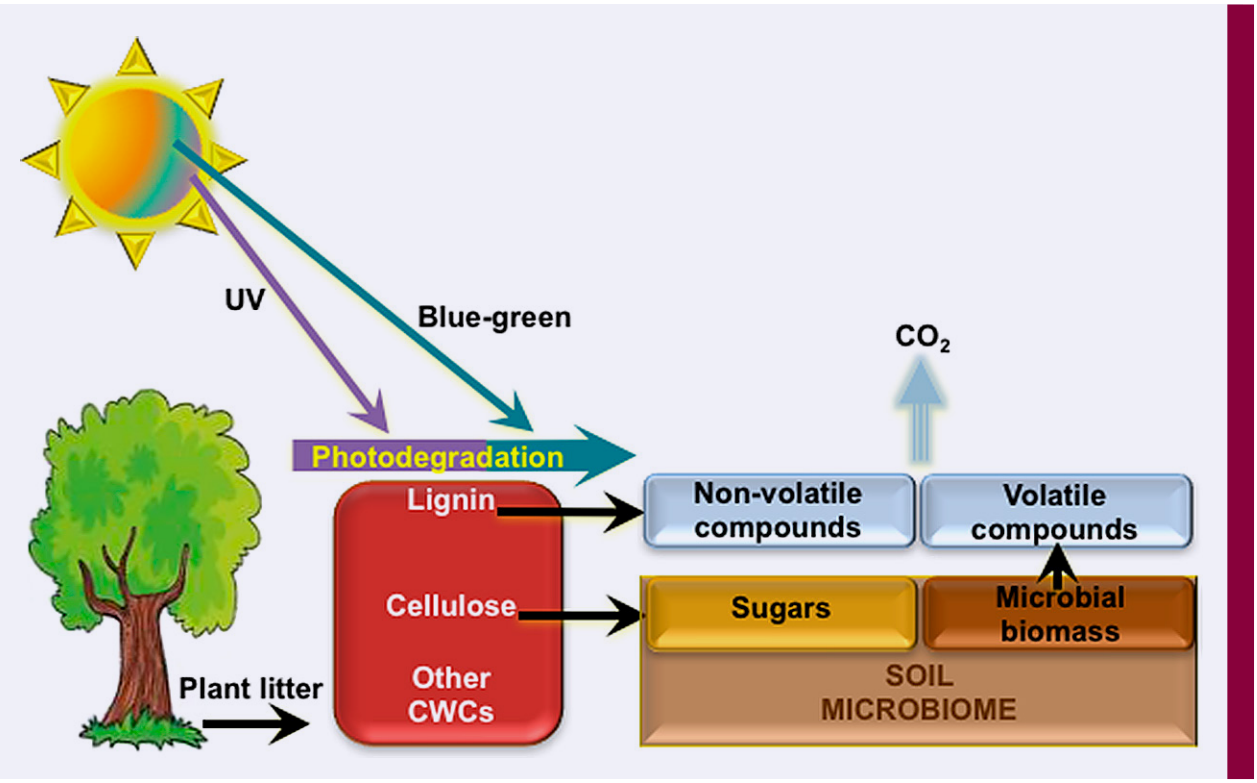

Fig. 7 **Conceptual model of the effects of solar radiation on litter degradation and microbial decomposition in terrestrial ecosystems. UV radiation and blue-green light cause the direct breakdown of lignin, cellulose and other plant cell wall components (CWCs), forming non-volatile and volatile compounds, such as carbon dioxide (CO_2), the latter being released to the atmosphere. This abiotic process is often referred to as photomineralisation. The changes in litter substrate resulting from photodegradation enhance the microbial breakdown of litter through a process called photo-facilitation. UV photons in sunlight may also directly inhibit the activity of decomposing microbes. Figure adapted from ref.[25].**

turn, increase the ease with which microbes can decompose litter.[17, 22] This latter process is often called photo-facilitation or photopriming (see Chapter 5). However, solar UV radiation, especially shorter wavelength UV-B radiation, may also inhibit the activity of microbes and change the composition of the microbial community, which then works in opposition to photo-facilitation.[38, 190] The net effect of these mechanisms is modified by environmental conditions (e.g., availability of moisture) and the spectral quality of sunlight, which varies depending on stratospheric ozone depletion, cloud cover, pollution, and plant canopy.

Recent studies have shown that photodegradation (photochemical mineralisation plus photo-facilitation) occurs in a variety of environments,[17] but the mechanisms and quantitative importance of this process in driving the overall decomposition of litter remains unclear in many cases. Since UV radiation can also inhibit microbial activity, a shift in spectral composition (i.e., UV-B:PAR ratios) would likely change the balance between photo-facilitation and microbial inhibition. This may be one reason why some experimental and modelling studies fail to detect a relationship between photodegradation and lignin content of litter.[3, 190] Long-term studies indicate that increased rates of decomposition due to photodegradation become evident only in later stages of decomposition, as was found after four months for savannah litter in a controlled experiment,[189] and after 12 months in a semi-arid ecosystem.[331] This suggests that the availability of substrates to microbes is only noticeably increased by photo-facilitation once readily-available substrates in fresh litter have been depleted. A diel time period (i.e., 24 h) appears to allow microbes to benefit from daytime photo-facilitation, possibly recovering during darkness, as well as utilising the extra humidity at night.[120, 189]

Field studies continue to show that photodegradation contributes most to the acceleration of litter decomposition in hyper-arid (annual precipitation < 150 mm), arid, and semi-arid eco-systems.[145, 330] In two contrasting locations on the Mediterranean steppe, UV radiation increased the decomposition rate of grass and shrub litter in a continental climate, but not in a high rainfall maritime climate.[6, 120] These findings suggest that, in drylands, photochemical mineralisation dominates under the driest conditions, whereas photo-facilitation tends to dominate under slightly moister conditions. The acceleration of decomposition attributable to photo-facilitation can even be detected in sub-tropical and temperate environments in both litter and coarse woody debris.[348] However, when moisture levels are favourable enough to support high microbial activity, UV radiation can have negative effects on decomposition, presumably because of direct inhibitory effects of solar radiation on the microbial populations.[252]

The majority of field photodegradation studies to date have been conducted in ecosystems occurring in dry (arid and semi-arid) rather than moist (mesic) climates.[38] However, the interaction of moisture and photodegradation has recently been garnering attention.[120, 293, 330] In moist, forested ecosystems, the amount of solar radiation reaching litter through the canopy can alter decomposition rates.[202] Different types and densities of canopy affect both the amount of radiation reaching ground level and its spectral composition.[112] This implies that shifts in type of vegetation occurring because of changes in land-use and climate are likely to affect decomposition rates through photodegradation interacting with concomitant changes in temperature and moisture.[12, 55, 262] Typically, the encroachment of woody plants leading to conversion of grasslands to shrublands driven by climate change and/or land abandonment, will alter litter composition and chemistry. This will shift C:N ratios in litter, affecting not only microbial activity but also photo-facilitation of litter and direct photodegradation.[12, 52, 137] In addition to shifts in type of vegetation, the exposure of litter to solar radiation will be determined by plant morphology and functional strategy. In habitats

where standing dead litter remains on the plant, this will present a greater surface area exposed to sunlight than situations where litter falls to the ground becoming easily mixed with soil which then reduces photodegradation.[39, 136, 251, 330, 331]

The structure and biochemical composition of litter produced by different plant forms plays a significant role in determining the underlying rate of decomposition. Hence litter with high lignin content may decompose slowly and be most affected by direct photochemical degradation.[16, 103] However, variations in photodegradation among species independently of their lignin content,[166] suggest that other traits of litter are also important (see ref.[20] for additional discussion). The UV radiation received by plants during growth can affect leaf morphology and the amount and composition of phenolic compounds that accumulate in the leaf epidermis,[50] as well as affecting the rate at which leaves will break down. These traits may continue to modify the optical properties of the leaf and hence the extent to which solar radiation penetrates the leaf during the early stages of decomposition.[85] Likewise, the depth and density of litter, its physical movement (e.g., by wind, rain), and the degree to which litter mixes with soil will determine the surface area exposed to sunlight, factors that are likely to be highly important for photodegradation.[38, 166]

The insight that recent research brings into the role of UV radiation and short-wavelength visible light in photodegradation in humid temperate as well as arid biomes,[5, 70] means that photodegradation has the potential to modify processes such as carbon cycling across many biomes. This broader relevance compared with our past knowledge of photodegradation extends its scope to affect the biogeochemistry of terrestrial ecosystems under climate change and with future stratospheric ozone recovery (Chapter 5).

7 Climate change is altering the exposure of organisms to UV radiation

Previous assessments have focused on the effects of ozone-driven changes in UV-B radiation.[50] However, climate change is increasingly exerting a stronger control on UV-B and UV-A radiation received by organisms as a result of changing cloud cover, vegetative cover, shifting of geographic ranges of species, changing of seasonal timing of growth and reproduction, and migration. Some of the potential implications of these climate-driven changes in exposure to UV radiation for terrestrial organisms and ecosystems are addressed below.

7.1 Species migration, UV radiation, and climate change

Plants and animals are shifting their ranges to higher latitudes and elevations in response to climate change and additional changes in distributions are expected to occur in the future.[83, 149, 257] However, species vary in their potential rates of migration. For plants, short-lived, herbaceous species (grasses and forbs) generally shift geographic ranges more rapidly than long-lived, woody species (trees and shrubs).[149] Non-native (i.e., introduced) species of plants also appear to exhibit higher migration potentials than native (i.e., indigenous) species.[83, 347] These climate change-driven shifts in geographic ranges will likely alter the exposure of plants to UV-B radiation, since UV-B irradiances generally increase with increasing elevation and decrease with increasing latitude.[21, 48, 62] However, these changes in plant exposure to UV-B radiation will not occur in isolation of other environmental factors, since a number of abiotic

(e.g., temperature and moisture) and biotic (e.g., associated pests, pathogens, and competitors) factors change with the migration of organisms to higher latitude and elevation.[149, 169] Consequently, these shifts in geographical range will likely expose organisms to unique combinations of UV radiation and co-occurring environmental factors. To what extent UV radiation plays a role in influencing migration patterns and how plants and animals respond to different conditions of UV radiation in the context of these other environmental changes as they migrate, has received little attention to date (but see section 3). However, certain insights into these effects can be gleaned from studies comparing plant populations or ecotypes whose distribution naturally spans a range of latitudes or elevations.

Plants that are adapted to grow in high elevation environments (i.e., alpine) often accumulate more UV-screening compounds (e.g., flavonoids) and have other UV-protective mechanisms compared with those plants occurring at lower elevations.[117, 227, 304, 333, 360] These differences are likely the result of the combined effects of elevational changes in UV radiation, temperature and other factors.[4] As discussed in section 3.4, low temperatures induce the production and accumulation of flavonoids. This may then increase levels of UV-screening and protection against oxidative stress.[167, 182, 337] High- and low-elevation plant populations may also differ their abilities to acclimate to changes in UV radiation.[332] In wild potatoes *(Solanum kurtzianum),* populations grown at low elevation have relatively low constitutive (base-line) levels of leaf flavonoids but a high capacity for induction of flavonoids when UV radiation increases. In contrast, plants at high elevations have high constitutive flavonoid levels, but do not necessarily increase their UV-screening in response to supplemental UV-B radiation in experimental studies.[147] Differential sensitivity to UV radiation of high *vs* low-elevation populations may also be due, in part, to population differences in DNA damage and repair, as has been shown for *Arabidopsis*.[332]

Whether there are differences in tolerance to UV radiation between native *vs* introduced species is unclear at present. For example, introduced populations of Chinese tallow tree *(Triadaca sebifera),* taken from south-eastern USA where the species was introduced in the 1700s, were shown to be more sensitive to UV-B radiation than native Chinese populations.[329] By comparison, no differences were found in the sensitivity of seed germination to UV-B radiation in native *vs* introduced populations of *Verbascum* and *Echium* in New Zealand.[139] Similarly, native and non-native species showed similar levels of UV-screening when growing in a high UV, tropical alpine location.[36] However, UV-screening increased with increasing elevation and UV-B radiation in a non-native species (*Verbascum thapsus* (mullein)) but did not vary with elevation in the native *Vaccinium reticulatum* ('ohelo). In contrast, similar levels of phenotypic plasticity (acclimation potential) between native (German) and non-native (New Zealand) populations of *Hieracium pilosella* with respect to morphological and growth response to UV-B radiation under growth chamber conditions have been found.[40] Thus, while it is generally assumed that non-native species can acclimate more readily to environmental change than native species,[84] it is unclear whether this generalisation applies to tolerance to UV-B radiation. Plants expanding their distribution into higher latitudes, would be expected to experience less exposure to UV-B radiation. As already noted, this may then lead to a decline in UV-screening compounds, antioxidants and other metabolites involved in photo-protection.[67]

To date, relatively little research has exploited remote sensing to make quantitative assessments of plant responses to elevation and climate change. However, the potential to use this approach is apparent from remote sensing images of a 1-hectare area (from the Carnegie Airborne Observatory-2), using a high-fidelity visible-to-shortwave infrared (VSWIR)

imaging spectrometer and dual laser waveform (LiDAR), which was calibrated against spectrophotometric measurements of leaf extracts.[14] This allowed a trend to be identified for increased phenolics with elevation (excluding the upper-most measurement point) using LiDAR images at the landscape scale in the Peruvian Andean rainforest. As this approach becomes more widely adopted, it will enable the resolution of large-scale relationships with topography and climate, allowing patterns in response to UV radiation and climate change to be mapped using remote sensing of large areas. Unmanned aerial vehicles (drones) are also increasingly being used to bridge the gap between satellites and ground measurements and to measure spectral reflectance at high resolution and under clouds.[204]

Ecosystems, and populations of plant species, including native species, have responded over the eons to changing environmental conditions. However, the recent rapid rate of climate change, in particular increasing temperatures and more frequent extreme weather events, are of concern in terms of the conservation of species and habitats.[257] Understanding the role of UV radiation in shifting distribution patterns and how readily plant populations can adjust physiologically and genetically to new UV radiation environments is therefore relevant to the conservation of biodiversity and the services that these natural ecosystems provide to humans.

7.2 Clouds, canopies, and plant response to fluctuating UV radiation

Climate change is altering cloud cover with some regions experiencing increased and other regions decreased cloud cover (Chapter 1 and ref.[149]). The effect of clouds on UV radiation also depends on the type of clouds[200] as well as their position relative to the sun.[106] These changes in cloud cover alter the long-term (days to weeks) exposure of plants to UV radiation and they can also change the short-term (seconds to hours) dynamics of UV radiation received by plants. (**Fig. 8**; ref.[106]) Whereas considerable attention has been given to understanding plant

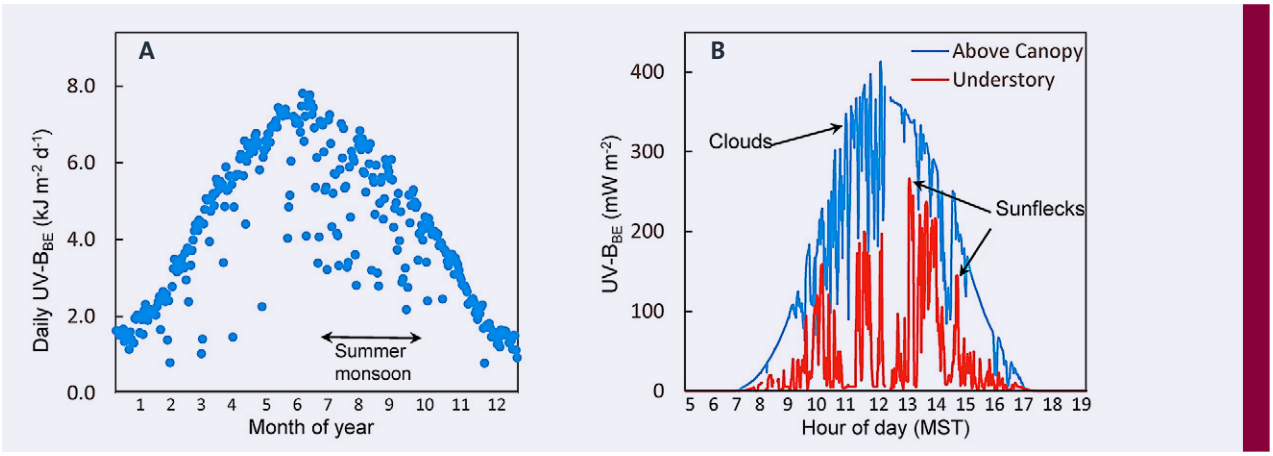

Fig. 8 **Variability in ground-level UV-B radiation over multiple time scales in the Sonoran Desert, USA. Panel A shows incident daily plant effective UV-B radiation over one year (January–December; months 1–12) with the annual summer monsoon (rainy and cloudy weather) indicated. Panel B shows instantaneous plant effective UV-B radiation over a single summer day measured above (blue line) and beneath (red line) a velvet mesquite *(Prosopis velutina)* canopy. Fluctuations in UV-B radiation in the understory result from changing cloud cover and the penetration of direct solar radiation through gaps in the canopy (sunflecks). Unpublished data from P.W. Barnes.**

responses to changes in average UV radiation conditions that occur over long time periods (see section 3.3, refs,[46, 50] and references therein), far less is known about plant response to rapid fluctuations in solar UV radiation. A number of studies have, however, demonstrated that concentrations of UV-screening compounds in mature leaves can vary over the growing season[237], from one day to the next,[303] over the course of an individual day,[33] and in response to rapid changes in clouds.[36] The changes in UV-screening that occur over the day are rapid (within minutes), reversible, and have been shown to be linked to changes in the content and composition of UV-absorbing compounds (flavonoids and related phenolics).[36] At present, the underlying mechanisms responsible for these rapid changes in UV-radiation protection are unclear, as is the significance of these changes for plant growth and function. These findings do; however, indicate that many, but not all, plant species can rapidly adjust their UV-screening in response to fluctuations in UV irradiances.[34]

The disruption of plant canopy structure (e.g., due to fire or drought-induced mortality of trees) alters the amount and spectral composition of sunlight penetrating canopies (i.e., ratios of UV-B:UV-A:PAR), but the specific changes depend on the type of canopy and vertical position (e.g., crown *vs* understorey).[23] Recent studies using array spectrometers have captured rapid changes in the sun-shade environment under canopies by recording multiple spectra every second.[128] These measurements at high temporal resolution have confirmed findings from earlier studies[59, 112, 122] that the spectral composition as well as total irradiance differs between sun flecks and understorey shade in forests and crop canopies. The importance of this fine-scale temporal and spatial variation in UV radiation in understorey environments for plant growth and development is not entirely clear at present (but see refs[173, 174]). There is evidence, however, that plants use the total irradiance received or modulated as cues,[192] which can prime them for seasonal or periodic changes. This may therefore be an important aspect of UV acclimation in understorey species that could lead to better adjustment to conditions of variable UV radiation resulting from modified overstorey canopies brought about by climate change.

Light tends to penetrate canopies more effectively under overcast or hazy sky conditions when the ratio of diffuse to direct radiation is higher, than under clear sky conditions.[71, 92, 184] Thus, cloudy conditions produce short-term increases in photosynthesis at the whole canopy level.[228, 317, 318] However, because leaves that develop in the sun are more efficient in using direct than diffuse radiation, and efficiency of leaves that develop in the shade does not differ significantly under changing sky conditions[57], caution must be exercised in generalising from these results. Conclusions that plant productivity will be enhanced by projected increases in diffuse solar radiation resulting from manipulating aerosol levels in the atmosphere to reduce climate change (i.e., geoengineering, see Chapter 1) must be viewed with a high degree of uncertainty because they will depend on the geographic location, on the extent of the reduction in incident irradiance, and whether the increased canopy light-use efficiency from diffuse radiation is sufficient to offset this and persist in the long term.[346]

Remote sensing of vegetation using satellites is routinely used to measure primary productivity and leaf pigments involved in photosynthesis; this technique has been used extensively for the scaling of ecosystem processes related to the carbon cycle.[353] Most of these ecosystem process models have been developed for use in combining leaf-level and remotely-sensed data, but new possibilities to better understand canopy reflectance of UV radiation are being made possible by the capacity to extend these remotely captured images and spectral data into the UV range of the spectrum.

Radiative transfer models used to model canopy optical properties and determine the fate of solar radiation have not yet been extended into the UV range, e.g., the discrete anisotropic radiative transfer model.(DART [119]) These models can incorporate sub-models for leaf optical properties (e.g., PROSPECT-D[107] and Fluspect-CX[323]), which previously have been applied for optical estimation of chlorophyll and carotenoids but if extended into the blue light and UV-A regions could include estimation of anthocyanins[324] and flavonoids. This may be facilitated by the new generation of those satellites designed for monitoring vegetation, which include the capacity to detect wavelengths spanning into the UV portion of the spectrum (from the European Space Agency, 270–370 nm for Sentinel-5 Satellite and Sentinel-5-precusor satellite). An alternative approach is to extend atmospheric radiative transfer models, such as libRadtran (Chapter 1 and ref.[101]) and the tropospheric and visible solar UV radiation model (http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV), to include radiative transfer through plant canopies or even greenhouse structures in the same way that DART and other radiative transfer models (RTMs) are being applied for the visible spectrum, or even coupling these two model types together. At the leaf level, commercial sensors (e.g., Ocean Optics Jaz[123]) and custom-made devices (e.g.,[272]) have the capacity to measure leaf reflectance in the UV range in both broadleaved and needle-leaved plants.

In crop canopies, planting distance and crop species, or even the cultivar or variety planted, will dictate the canopy architecture and affect the spectral composition and total irradiance reaching the lower leaves. These decisions also have implications for how UV-B radiation affects plant growth and defence at the canopy level in agricultural crops (see ref.[24] and section 5.3). With a better understanding of the mechanisms by which plants in canopies respond to UV radiation as a part of the incident spectral irradiance over vertical profiles, we can make better-informed management decisions on species and cultivar selection for specific locations.

7.3 Phenology and UV radiation

The implications of warmer winters for the seasonal timing of development or phenology have been extensively studied, with findings consistently showing both the early emergence of animals[77, 307] and the earlier onset of plant growth.[74, 170] Although the molecular mechanisms controlling phenology are not fully understood[305], it is known that organisms often use a variety of environmental cues to safeguard against mis-timing of development.[175, 282, 362] Differences among life forms in their rate of response to temperature, which is usually the predominant cue, create the potential for a disruption of ecosystem processes through a mismatch in the timing of phenology among co-existing organisms such as plants and pollinators.[243, 264] It is likely that warmer temperatures will bring overwintering trees out of dormancy prematurely. This will produce an earlier spring bud-burst, possibly so early in the year that at high latitudes new leaves receive insufficient sunlight (and by definition less UV-B radiation) to develop as they normally would do later in the year.[45, 232] This forward displacement of phenology due to warming may also heighten the role of alternative phenological cues (e.g., daylength and spectral quality).[56, 339] In particular, more research is required to better understand interactions between daylength (photoperiod) and cues related to spectral quality (i.e., changes in UV-B, UV-A, blue and red light), both of which are detected by plant photoreceptors. Alterations in the timing of spring phenology, particularly at high latitudes, may expose understorey plants to new light environments in early spring when freezing temperatures may limit their physiological acclimation capacity.

8 Tracking changes in past UV radiation over geological timescales using the biochemical signatures of plants

The long-term ecological effects of UV-B radiation over geological timescales are studied by palaeoecologists interested in retrospectively reconstructing solar UV-B radiation. Identifying a reliable proxy for tracking changes in UV-B radiation based on the biochemistry of pollen and spores, would help interpretation of the effects of UV-B radiation on terrestrial ecosystems. However, even then an additional calibration would be required to separate changes in total solar radiation from those of UV-B radiation, and it would be difficult to distinguish whether these changes resulted mainly from stratospheric ozone depletion or other environmental or astronomical factors. Improvements in analytical techniques have reduced the uncertainty associated with reconstructions of solar radiation based on the biochemistry of pollen from ice cores and lake sediments that track changes in past UV radiation over geological time scales.[115, 224] These reconstructions may provide a better understanding of the evolution of the stratospheric ozone layer and its interaction with climate change.[158, 278] However, the extent to which UV-absorbing compounds in pollen can be considered reliable indicators of the past UV-B radiation and reflect changes at high temporal resolutions, depends upon the causative temporally-stable relationship between the accumulation of these compounds in pollen and exposure to solar UV-B radiation being experimentally verified.[308]

The preserved outer walls of fossilised spores and pollen grains are made from sporopollenin, which is highly resistant to degradation over geological time scales and contains the phenolic compounds, para-coumaric acid and ferulic acid. Experiments using supplemental UV-B radiation have found the concentrations of these compounds to be proportional to the incident solar UV-B radiation received by the pollen.[89, 278] Exploiting this relationship has enabled the reconstruction of UV irradiance at Lake Bosumtwi, in modern-day Ghana.[158] This work has shown that over a 140-thousand-year period, fluctuations in the concentration of phenolics from grass pollen contained in sediments corresponded with patterns of solar UV irradiance derived from changes in the Earth's orbit over cycles of 19–21 thousand years.[158] The correlation between reconstructed UV-irradiance and phenolic concentration is also evident from pine pollen[344] and spores of the ubiquitous clubmoss *Lycopodium*[197] over broad latitudinal gradients, although this correlation is more robust across local elevational gradients.[308] This is because seasonal and environmental variability and differences in UV-B radiation related to weather patterns (temperature and cloudiness) and canopy shade can confound the relationship.

The lack of standardisation and inter-comparability of samples and sampling techniques is one impediment to the wider use of the above techniques. Improvements in the two analytical approaches used to detect phenolic compounds, i.e., Fourier-Transform (FT) high-throughput infra-red spectroscopy and thermally-assisted hydrolysis methylation (THM) with pyrolysis-gas chromatography mass spectrometry (THM-GC/MS), should allow researchers to obtain more detailed information from pollen samples.[18, 157, 285] In the latter case, precision should also be improved by calibration of changes in phenolic compounds against a known concentration of a compound added to the sample as a standard or against another compound within the pollen that does not respond to changes in solar radiation.[285] When used in conjunction with radiative transfer modelling,[309] these approaches show promise in distinguishing past environmental gradients in UV radiation, such as that at the end of the Permian period (*ca* 250 million years ago),[49, 327] from other climate changes

across geographical gradients, and long time-scales. This has the potential to improve our knowledge of the causes and consequences of stratospheric ozone depletion.

9 Key gaps in knowledge

Current gaps in our knowledge of the linkages between stratospheric ozone, UV radiation and climate change and their implications for terrestrial ecosystems are a direct consequence of the complexity of systems characterised by interactive loops that link climatology, meteorology and biology (**Fig. 1**). The challenge lies in developing integrated approaches to assess the effects of UV radiation against a complex background of rapidly evolving environmental conditions and increasing human interventions. The way in which ecosystems respond to the often-interactive effects UV radiation and other climate change dynamics can have important consequences for the functionality and/or productivity of agricultural and natural ecosystems, but currently leave many unknowns. This emphasises the importance of studying combinations of those environmental factors that often change with UV radiation and which may modify the response of organisms to UV radiation in terms of acclimation and productive growth. Thus far, most research has concentrated on potential interactive effects of UV radiation with temperature and/or drought. Since climate warming continues to increase, a better understanding is needed of the effects of UV-B radiation and rising carbon dioxide together with other climate variables on natural and agricultural systems. This will then facilitate assessments of future outcomes for ecosystem functioning, conservation of species, and selection of environmentally suitable agricultural crops. While growth chamber studies can make valuable contributions to understanding some of the fundamental mechanisms of plant response to UV radiation, there is still a strong need for many growth chamber studies to be validated in the field for a realistic perspective of how organisms will respond in a more natural environment.

The balance between negative and beneficial effects on organisms will determine the current and future adaptation and sustainability of terrestrial ecosystems. Changing exposure to UV radiation and climate change factors will affect plant resistance to pests and diseases, food quality and nutritional quality, as well as potentially modifying the behaviour of terrestrial animals. These changes may also affect visual cues contributed by UV radiation for certain animals. However, more information is required to evaluate the possible implications in the context of animal response to future environments and in plant-pest and plant-pollinator interactions, which will have a bearing on food security.

While qualitative analysis of responses to UV radiation and other variables is usually possible, quantitative analyses are often lacking due, in part, to the complexity of diverse and constantly changing biological systems. For example, it is difficult to quantify the importance of processes such as photodegradation and microbial breakdown of terrestrial plant litter for soil carbon storage and emissions at regional and global scales, and their potential contribution to global warming and nutrient cycling.

Climate change together with changes in land-use will very likely continue to have strong impacts on the exposure to UV radiation of ecosystems and terrestrial organisms, including human populations. On a global scale, there is currently insufficient information on the relative contribution and implications of stratospheric ozone depletion to climate change in the southern hemisphere, and how much can be attributed to natural variability. These interactive effects need to be evaluated for the way in which they may continue to modify ecosystem response in a future with a recovering stratospheric ozone layer. In addition,

emerging findings from monitoring of stratospheric ozone need to be taken into account for evaluating the possible implications of any sudden change towards the projected path of ozone recovery. This was recently illustrated in a report[229] suggesting that there are unexpected indications that emissions of the banned ozone-depleting compound, chlorofluorocarbon-11 (CFC-11), have increased. The magnitude and future significance of the responses of terrestrial ecosystems to increasing or decreasing UV radiation, either dependent or independent of stratospheric ozone depletion, and in the context of climate change, remain largely unknown.

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4 The interactive effects of ozone depletion, UV radiation, and climate change on aquatic ecosystems

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Summary

This report summarises the current state of knowledge on the interactive effects of ozone depletion and climate change on aquatic ecosystems, focusing on how these affect exposures to UV radiation in both inland and oceanic waters. The ways in which stratospheric ozone depletion is directly altering climate in the southern hemisphere and the consequent extensive effects on aquatic ecosystems are also addressed. The primary objective is to synthesise novel findings over the past four years in the context of the existing understanding of ecosystem response to UV radiation and the interactive effects of climate change. If it were not for the Montreal Protocol, stratospheric ozone depletion would have led to high levels of exposure to solar UV radiation with much stronger negative effects on all trophic levels in aquatic ecosystems than currently experienced in both inland and oceanic waters. This "world avoided" scenario that has curtailed ozone depletion, means that climate change and other environmental variables will play the primary role in regulating the exposure of aquatic organisms to solar UV radiation. Reductions in the thickness and duration of snow and ice cover are increasing the levels of exposure of aquatic organisms to UV radiation. Climate change was also expected to increase exposure by causing shallow mixed layers, but new data shows deepening in some regions and shoaling in others. In contrast, climate-change related increases in heavy precipitation and melting of glaciers and permafrost are increasing the

concentration and colour of UV-absorbing dissolved organic matter (DOM) and particulates. This is leading to the "browning" of many inland and coastal waters, with consequent loss of the valuable ecosystem service in which solar UV radiation disinfects surface waters of parasites and pathogens. Many organisms can reduce damage due to exposure to UV radiation through behavioural avoidance, photoprotection, and photoenzymatic repair, but meta-analyses continue to confirm negative effects of UV radiation across all trophic levels. Modeling studies estimating photoinhibition of primary production in parts of the Pacific Ocean have demonstrated that the UV-B radiation component of sunlight leads to a 20% decrease in estimates of primary productivity. Exposure to UV radiation can also lead to positive effects on some organisms by damaging less UV-tolerant predators, competitors, and pathogens. UV radiation also contributes to the formation of microplastic pollutants and interacts with artificial sunscreens and other pollutants with adverse effects on aquatic ecosystems. Exposure to UV radiation can decrease the toxicity of some pollutants such as methyl mercury (due to its role in demethylation) but increase the toxicity of other pollutants such as some pesticides and polycyclic aromatic hydrocarbons. Feeding on microplastics by zooplankton can lead to bioaccumulation in fish. Microplastics are found in up to 20% of fish marketed for human consumption, potentially threatening food security. Depletion of stratospheric ozone has altered climate in the southern hemisphere in ways that have increased oceanic productivity and consequently the growth, survival and reproduction of many sea birds and mammals. In contrast, warmer sea surface temperatures related to these climate shifts are also correlated with declines in both kelp beds in Tasmania and corals in Brazil. This assessment demonstrates that knowledge of the interactive effects of ozone depletion, UV radiation, and climate change factors on aquatic ecosystems has advanced considerably over the past four years and confirms the importance of considering synergies between environmental factors.

1 Introduction

The effects of ultraviolet (UV) radiation on aquatic ecosystems and associated security of food and water depend strongly on interactions with climate change including warming, cloudiness, precipitation patterns, ice and snow cover, as well as other environmental factors such as clarity of water, acid-deposition, and acidification of oceans (**Fig. 1**). These interactive effects control the levels of underwater exposure to UV radiation as well as the ability of organisms to respond to damaging UV through behavioural avoidance, production of photoprotective compounds, and repair mechanisms. Indirect effects of UV radiation on aquatic organisms are also important through their influence on predators, competitors, parasites, and pathogens, as well as on access to food resources and optimal habitat. For example, one of the most valuable ecosystem services provided by solar UV radiation is that the most damaging, shortest wavelengths also contribute to solar disinfection of waterborne parasites and pathogens that can reduce disease of many organisms. Reductions in the clarity of water associated with natural and anthropogenic activities can compromise these critical ecosystem services. Here we provide a current assessment of knowledge about the effects of UV radiation on aquatic ecosystems, emphasising the novel findings since the last United Nations Environment Programme's Environmental Effects Assessment Panel Quadrennial report.[89] We start by assessing recent advances in understanding of the major factors controlling underwater exposure to UV radiation, and then discuss both the beneficial and

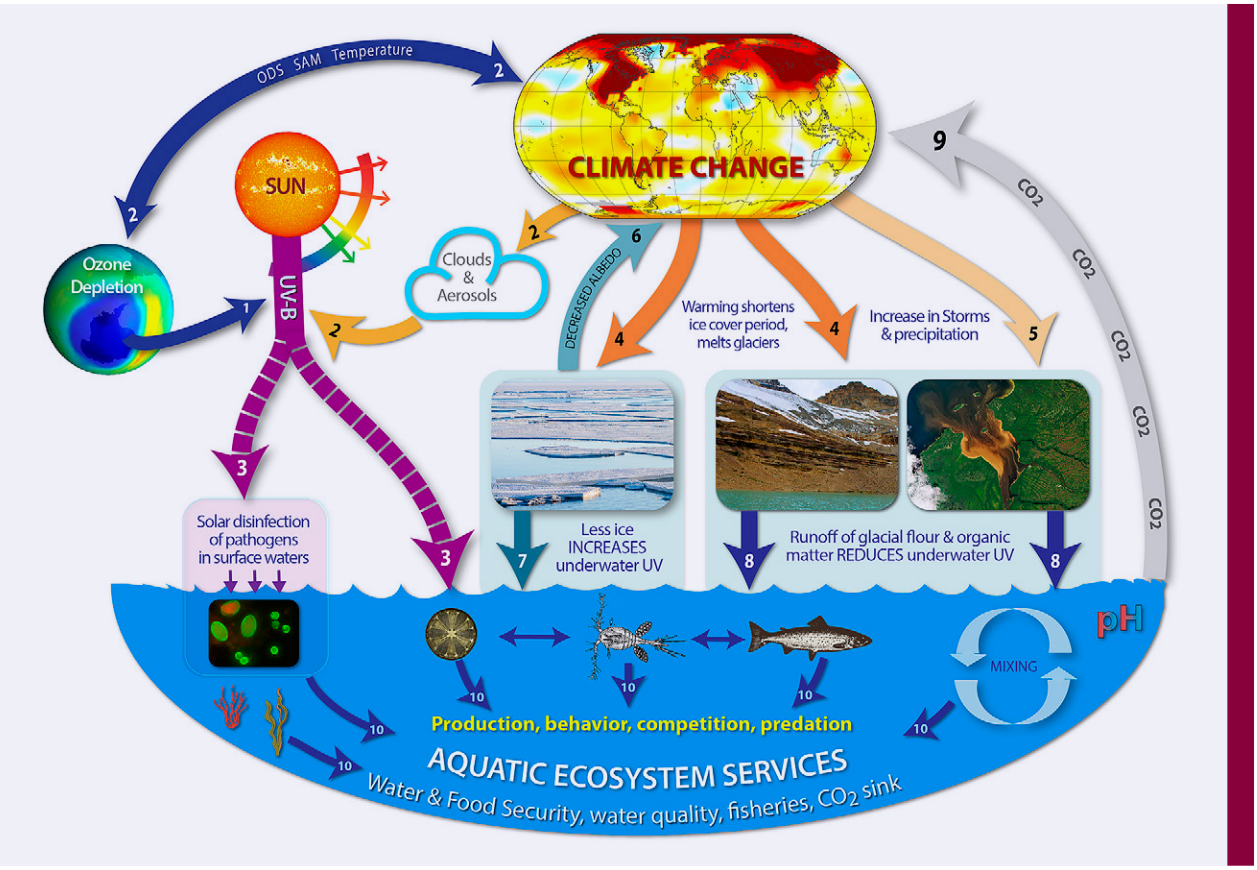

Fig. 1 **Conceptual diagram of (1) the direct effects of ozone depletion and (2) interactions with climate change, on (3) the amount of UV radiation that reaches the surface of aquatic ecosystems. Also shown are (4–9) the factors regulating underwater UV exposure and interactions with climate change, and (10) their consequent effects on aquatic ecosystem services. Climate warming is causing (4) shorter duration and thinner ice and snow cover and melting of glaciers, as well as (5) heavier precipitation that increases inputs of terrestrially derived dissolved organic matter (DOM) to aquatic ecosystems in many regions. Droughts reduce runoff and DOM inputs. Reduced snow and ice cover (6) decreases albedo (reflection back into space) and (7) increases underwater UV exposure, while increases in runoff from melting glaciers and increased DOM (8) reduce underwater UV exposure. Increases in atmospheric CO_2 (9) lead to acidification of aquatic ecosystems. Collectively these changes in the transparency of water can alter penetration of visible and infrared light that alter thermal stratification and thus mixing depth and consequent UV exposure of both attached and open-water aquatic organisms (see Fig. 2). Increases in DOM associated with declines in anthropogenic acid deposition and increases in precipitation may (8) increase pH in inland waters, while (9) increases in atmospheric CO_2 can decrease the pH in the oceans and some lakes, altering the role of these ecosystems as sinks or sources of CO_2, and increasing damage by UV radiation of calcifying organisms. These interactions between UV radiation and climate change modify (10, left to right) large algae, pathogens, aquatic food webs, and mixing processes, with important consequences for water and food security. Abbreviations: ODS, ozone depleting substances; SAM, Southern Annular Mode; UV-B, ultraviolet B radiation; CO_2, carbon dioxide. (Numbers in parentheses refer to the arrows in the diagram)**

adverse effects of UV radiation in the context of interactions with climate and other environmental change. We also discuss the unique climatic effects of ozone depletion over Antarctica on aquatic ecosystems in the southern hemisphere and provide an assessment of critical knowledge gaps in our current understanding of the effects of ozone depletion and UV radiation on aquatic ecosystems.

2 Changes in physical ecosystem structure alter exposure to underwater UV radiation

Climate change and stratospheric ozone depletion are changing exposure to UV radiation in marine and inland surface waters through their influence on incident irradiance, ice and snow cover, water transparency, and the depth to which organisms passively circulate. These factors modify habitat structure and the exposure of materials and organisms to solar radiation including UV radiation. The highest exposure levels occur in surface waters. This is especially true for short wavelength UV-B radiation, which is the most damaging per photon, but also the most strongly and selectively absorbed in natural waters. Vertical mixing moves organisms through surface waters of uniform temperature, commonly defined as the mixed layer depth. In inland waters, coastal zones, and open oceans, the mixed layer depths vary seasonally, regionally, and with water body characteristics. In the oceans, mixed layer depths are deeper in winter in polar regions, and shallower in coastal and tropical regions as well as in all waters during the summer.[147] They range from hundreds of meters at the deep, extreme depths, well beyond the penetration of solar radiation, to meters at the shallow extreme, in which exposure to UV radiation can be sufficient to cause significant effects.

The mixed layer depths of inland waters are extremely variable from centimeters to hundreds of meters, and are often deeper in more transparent lakes and reservoirs due to deeper penetration of visible and infrared wavelengths of sunlight.[69, 172, 184] Exposure to UV radiation can also be a factor in the vertical distribution of bottom-dwelling organisms. For example, water transparency to UV-B radiation is one component determining the upper depth distribution of marine, especially polar, macroalgae.[246]

2.1 Factors controlling exposure to UV radiation

2.1.1 Incident irradiance

Factors important in controlling incident UV irradiance, including stratospheric ozone, cloudiness, and aerosols, are discussed extensively in Chapter 1. Among these, there are some processes that alter incident irradiance that have specific importance to aquatic ecosystems, such as the influence of fires due to intensified droughts. Smoke from fires preferentially filters out UV radiation relative to visible light[229] (see also Chapters 1, 5, and 6), affecting many processes. Thus, when winds brought a smoke plume from large California wildfires over Lake Tahoe, zooplankton, which use UV radiation as a depth cue,[75] migrated to shallower depths, potentially affecting their susceptibility to plankton-eating fish predators.[212]

2.1.2 Ice and snow cover

The reduction in extent and duration of ice cover is one of the most widely recognised effects of climate change.[115] Ice cover is thinner and melts earlier than it has in the past in inland and coastal waters,[19, 51, 133, 196] and is covering less of the Arctic Ocean.[41] Depending on thickness, snow-cover on ice can prevent most or all UV radiation from entering the water column. Models predict that the decline in ice cover will cause as much as a 10-fold increase in UV-B radiation entering Arctic surface waters.[78] Simultaneously, photosynthetically active radiation (PAR, 400–700 nm) will increase, promoting increased production. Without ice, the water is also affected by wind, which enhances mixing. The increase in exposure to UV radiation can be quite large for higher latitude regions, where the ice-out occurs close to the summer solstice and the annual solar maximum when incident solar radiation is greatest.

Earlier and longer seasonal exposure to UV radiation could adversely affect key marine zooplankton[107] and accelerate the release of CO_2 to the atmosphere by photodecomposition of dissolved organic matter[47] (see Chapter 5) for more details on photodecomposition). A related effect of prolonged exposure to sunlight is photobleaching, which decreases the colour of terrestrially derived, dissolved organic matter (DOM), and increases the transparency of water to UV radiation.[10, 99, 156]

Around Antarctica, poleward displacement of climate zones is changing the size and distribution of the seasonal ice zones, most notably a loss of sea-ice around the Antarctic Peninsula, along with an increase in sea-ice in the Ross Sea.[43] The direction of this sea-ice change in the future, however, remains uncertain[103] (see Chapter 1).

2.1.3 Water transparency

Transparency of surface waters to UV radiation is primarily controlled by the amount of DOM, which, together with other constituents, is also an important regulator of transparency to visible light. DOM is increasing in many temperate waters in the northern hemisphere,[140] leading to decreases in transparency to UV radiation.[230] For example, 68% of 474 lakes sampled in Norway, Sweden and Finland show a median increase of 1.4% per year in total organic carbon (TOC) between 1990–2013.[54] This "browning" is caused by many factors, including increases in precipitation, change in land cover, and the recovery from acid deposition in some regions.[118] Browning is well documented in inland water bodies, such as lakes and reservoirs, with effects at least transiently reaching into nearshore ocean waters.[16, 72, 141] The ongoing browning of lakes is projected to continue if precipitation continues to increase,[54] and lakes with a retention time of 1–3 years may be especially affected by climate change-induced browning.[222] Increases in the inputs of terrestrially-derived DOM also increase absorption of longer wavelength visible and infrared sunlight, which warm the surface waters, leading to shallower mixing depths. This is particularly important in small water bodies.[165]

Like DOM, iron-containing compounds selectively absorb UV radiation and have been increasing in many inland water bodies. Increases in concentrations of dissolved iron have been observed in 28% of 340 water bodies examined in 10 different countries across northern Europe and North America.[20] These increases in dissolved iron are often associated with increases in DOM and similarly contribute to browning of inland waters. Increases in iron likely are contributing to reductions in the UV transparency of inland waters.[167] The role of UV radiation and iron biogeochemistry is addressed in more detail in Chapter 5.

Melting glaciers, thawing permafrost, and heavy precipitation events are also major causes of reductions in transparency of water to UV radiation; droughts have the opposite effect on water transparency.[229] Thawing of permafrost is a major source of DOM transported to Arctic lakes and rivers, the latter transporting DOM into the Arctic Ocean.[71, 72, 134, 201, 216] The transparency of surface waters also decreases due to silty water flowing from melting glaciers.[106, 182, 205] Extreme weather, which has increased in frequency with climate change, also affects the transparency of water by increasing runoff and transport of particles to surface waters. Transparency decreases when floods discharge large quantities of DOM and sediment into inland and coastal waters.[54, 95, 96, 203] On the other hand, drought is associated with increased transparency to solar radiation, including UV radiation, in lakes in both eastern and western United States, including Lake Tahoe.[229]

2.1.4 Mixed layer depth

Many organisms in open-water aquatic systems are planktonic. These are small organisms such as viruses, bacteria, phytoplankton, protozoa and zooplankton, which are passively carried as water circulates both vertically and horizontally in surface waters. Exposure of these organisms to UV radiation depends on their vertical position in the water column, as well as on the transparency of the water. Where it occurs, shallowing of the mixed layer depth can increase exposure of organisms to UV radiation by trapping them near the surface. The mixed layer depth responds to multiple climatic factors undergoing change, most importantly global warming, wind strength and distribution, and inputs from runoff and ice melt.[200] Decreases in the density of surface water due to warming and/or freshwater inputs into oceans encourage formation of shallow mixed layers, while strong winds and/or surface cooling break down density gradients, forming deeper mixed layers.

Early Coupled Ocean-Atmosphere Simulation models of global climate change predicted that global warming would increase stratification and, as a consequence, shallowing of mixed layer depths was expected.[18, 24] However, recent examination of long-term trends in observed ocean and mixed layer depths of lakes have not revealed any consistent global long-term trends. Instead, changes are regionally and/or seasonally specific.[116, 200] The discrepancy with model predictions is at least partly due to problems in properly incorporating wind-forcing into these models.[185] For coastal or inland waters, the role of weather and land-use changes in altering water clarity and thus the heat budgets can also be important.[165, 184] Higher resolution, regional simulations of the Southern Ocean predict latitude-specific changes in marine mixed layer depths, with shallower depths at the northern and southern limits of the Southern Ocean and deeper mixed layer depths in between[58] (**Fig. 2**). The deeper mixed layer depths are related to the strengthening of zonal winds associated with the dominance of the positive phase of the Southern Annular Mode (SAM), during which the latitudinal gradient in surface air pressure is intensified by stratospheric ozone depletion over Antarctica (**Fig. 2** and see section 6, and Chapters 1 and 3). Latitudinal shifts in climate zones associated with the positive SAM phase have a number of other consequences for southern hemisphere marine ecosystems, such as affecting nutrient supply to the surface layer and distributions of animals and bottom-dwelling organisms.[58] These effects are discussed in more detail in section 6.

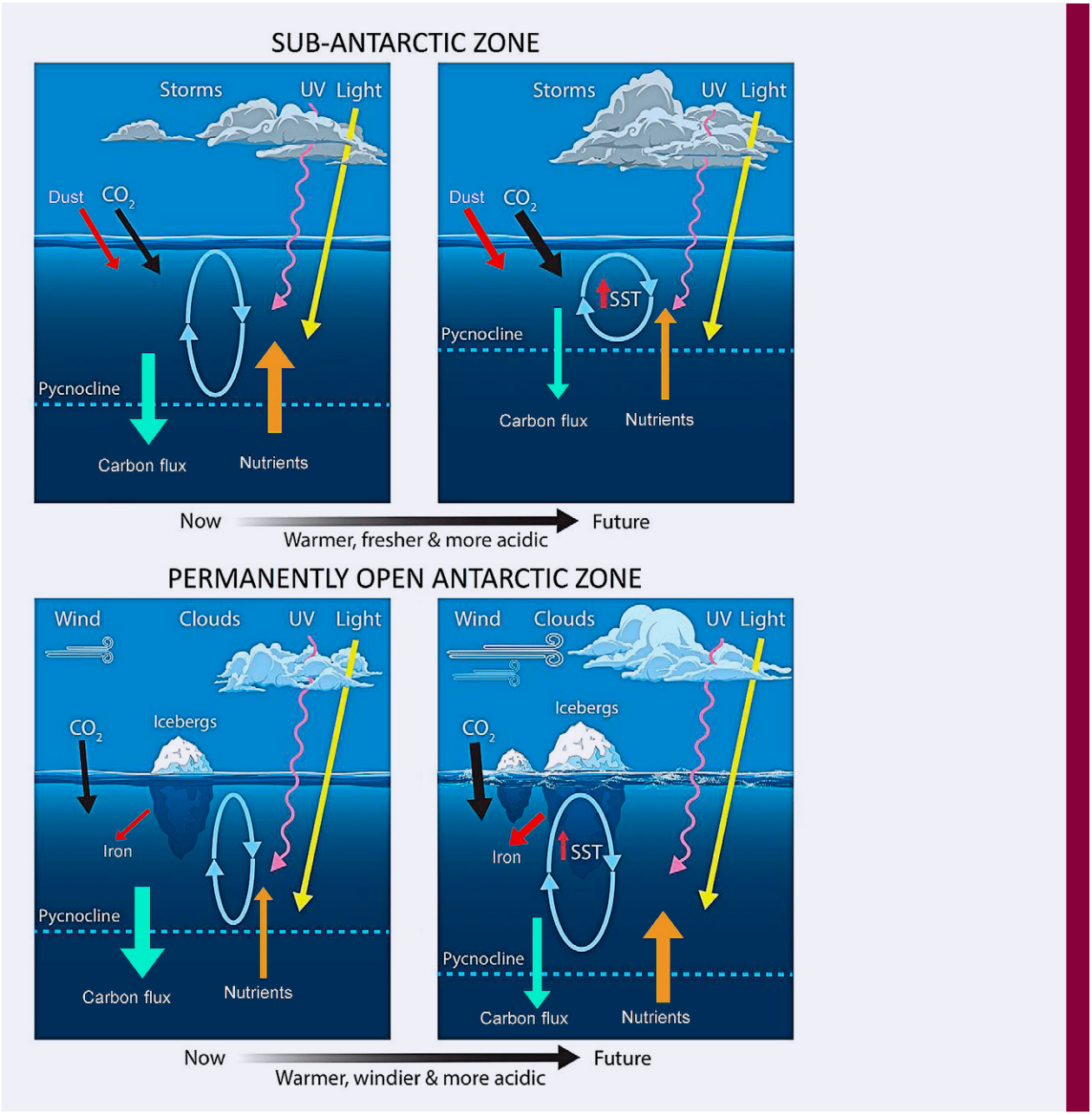

Fig. 2 **Illustration of how the interaction of factors influenced by global change has contrasting effects on sea surface temperature (SST), the density gradient (pycnocline, preventing mixing of surface waters with deeper waters), and exposure to UV radiation in different zones of the Southern Ocean. Climate models predict that the waters in the sub-Antarctic zone will become warmer, fresher, and more acidic, leading to more exposure to UV radiation in the surface layer despite increased cloudiness (top panel). Waters in the permanently open Antarctic zone will experience more acidity but less temperature rise and more wind and cloudiness, leading to deeper mixed layers and on average, less exposure to UV radiation (pink arrow) in the surface layer (bottom panel) CO_2, carbon dioxide. After Deppeler and Davidson.[58]**

The transparency of water is an important factor controlling mixed layer depth in smaller lakes, particularly those with areas of less than about 5 km² [69, 165, 172, 184] (**Fig. 3**). As water transparency decreases, visible and infrared light do not penetrate as deeply, confining heating to surface waters, potentially increasing the strength of thermal stratification. Therefore, the phenomenon of browning will likely decrease the mixing depth in many lakes (**Fig. 3**). However, this does not necessarily translate into increased exposure to UV radiation in the mixed layer because at the same time, UV radiation is strongly absorbed by the DOM. The decrease in the UV radiation from this filtering effect can outweigh the increase in average UV radiation with a shallower mixed layer (**Fig. 3**). Thus, browning is expected to decrease average exposure to UV radiation in many systems even though the surface layer is shallower.[98]

In summary, the combined effects of global change on exposure to UV radiation vary across different types of aquatic ecosystems. In some cases, exposure to UV radiation is increasing, while in other cases it is decreasing. The implications are multifold. Often, increases in exposure to UV radiation are associated with decreased plankton productivity and survival, while decreases can affect depth distributions (relevant to fisheries), and pathogen and parasite survival (relevant to human health). These responses are discussed in more detail in subsequent sections.

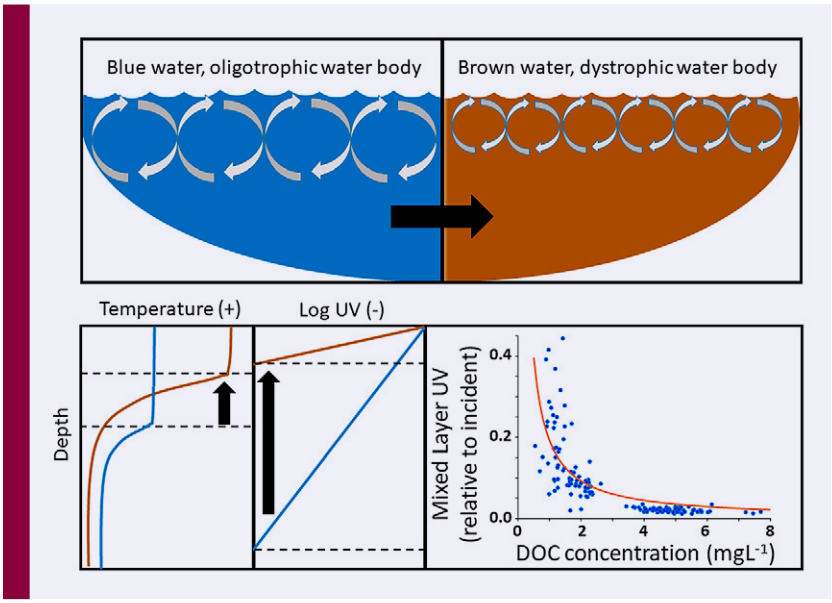

Fig. 3 **Browning (increased dissolved organic carbon, DOC) in smaller lakes (< 5 km²) reduces both mixing depth (top and bottom left panels) and UV transparency (bottom middle panels). As the surface layer absorbs more visible and infrared light, heating shifts closer to the surface and the mixed layer depth becomes shallower (short black arrow), affecting temperature profiles. However, UV radiation is more strongly absorbed by the DOC (UV profiles), and the decrease in the depth of penetration of UV radiation from this filtering effect (long black arrow) can outweigh the increase in average UV radiation related to a shallow mixed layer. The plot on the lower right shows average UV irradiance (red line) in the mixed layer (relative to incident UV) *vs* DOC (blue dots), based on 320 nm-UV profiles, surface layer depth from temperature profiles, and DOC measured in various lakes and times of the year (n = 148 samples, mainly from lakes in the northeast region of Pennsylvania, USA, from Williamson *et al.*[230]). Average UV radiation declines steeply over the range of 0–2 mg L^{-1} and much more gradually for concentrations of DOC over 4 mg L^{-1}. The generality of this relationship for other lakes is under investigation.**

3 UV radiation and interactions with climate change have adverse effects on aquatic organisms and processes but adaptations often reduce damage

UV radiation has been affecting the Earth throughout evolutionary time and organisms have developed adaptations to cope with this threat. The thinning of the stratospheric ozone layer and consequent changes in exposure to UV radiation over recent decades (see Chapter 1) has spurred efforts to quantify the adverse effects of UV radiation on aquatic organisms. The variety of behavioural, physiological, and evolutionary responses to UV radiation are also important considerations in quantifying the net effects of exposure to UV radiation at the ecosystem level, including changes in biodiversity.

Several recent meta-analyses confirm and extend our knowledge of the adverse effects of UV-B radiation on all trophic levels in both freshwater and marine ecosystems.[13, 130, 163] UV-B-exposure leads to elevated mortality but also sub-lethal adverse effects on reproduction, development, growth, behaviour and metabolism.[13, 130, 163]

However, some caution in interpreting these meta-analyses is necessary because many of the studies were conducted in laboratory settings and the spectral composition of the UV treatment was not considered (see also Chapter 3, section 3.3.1 for terrestrial ecosystem examples). Spectral composition is important because shorter wavelengths of UV radiation are many times more biologically damaging per photon than are the longer wavelengths (**Fig. 4**). The spectral dependence of the impacts of UV radiation differs among biological and chemical processes (**Fig. 4**). The spectral composition of irradiance in the aquatic environment is also variable, depending on depth and which factors control exposure (**Fig. 4**). Shorter wavelengths tend to be over-represented in laboratory studies, which generally have shown larger responses (i.e., stronger effects of UV radiation) compared to field studies.[163] Hence, while general adverse effects of UV-B radiation on aquatic organisms have been clearly documented, the strength of these effects in nature cannot be effectively estimated from experiments with artificial UV radiation unless spectral dependence is also quantified and taken into account. Thus, more attention to the spectral dependence of both exposure and response to solar UV radiation will be required to quantify the long-term effects of elevated UV radiation, especially on trophic interactions such as competition and predation. Shifts in trophic interactions can subsequently result in changes in community structure, ecosystem services, and food and water security.

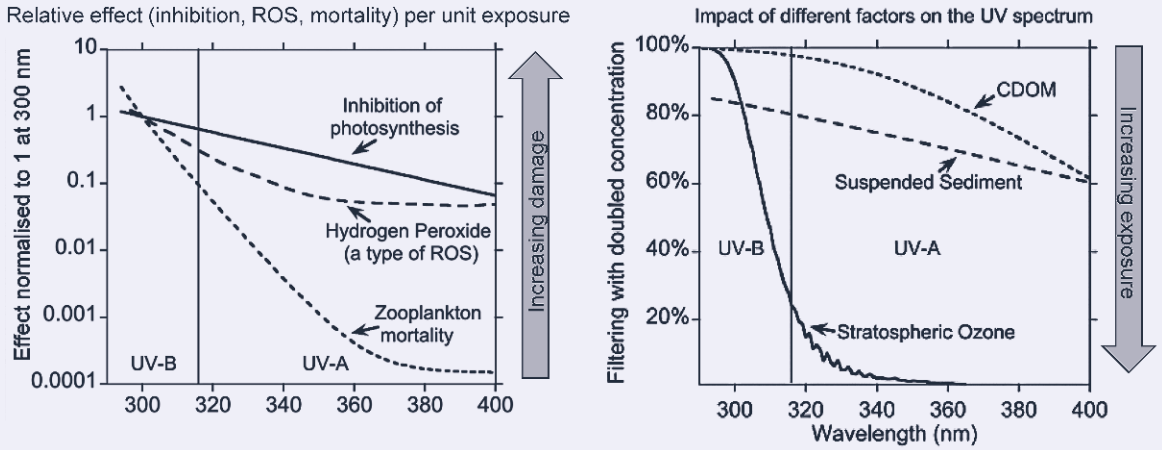

Fig. 4 **Spectral variation in some of the effects of UV radiation in aquatic ecosystems (top graph) compared to the spectral change in irradiance caused by different environmental factors (bottom graph). Effects are on a log scale and the wavelength ranges are divided between UV-B and UV-A. The top graph shows examples of the relative effectiveness of UV radiation at a specific wavelength in producing (1) dissolved hydrogen peroxide, a reactive oxygen species[113] (ROS), (2) inhibiting photosynthesis in picocyanobacteria,[151] very small phytoplankton characteristic of the central ocean, and (3) contributing to the mortality of freshwater zooplankton, small invertebrates and larval fish.[190] The bottom graph shows the filtering of UV entering the aquatic environment associated with a doubling of different UV-filtering substances, including stratospheric ozone, which filters incident irradiance,[132] while suspended sediment and coloured dissolved organic matter (CDOM) change water transparency.[183] For example, a filtering effect of 90% means that the doubled concentration has reduced irradiance to 10% compared to the original concentration. Aquatic ecosystems respond to both UV-B and UV-A radiation. Ozone specifically filters out UV-B radiation, while DOM strongly filters out UV-B radiation, but also reduces UV-A radiation and some visible light (wavelengths > 400 nm). Filtering by suspended sediment is not as wavelength-selective and reduces transparency in the UV-A and visible range. The curves are examples drawn from recent research, to illustrate the relative differences in spectral responses within aquatic ecosystems. It should be noted that these responses do differ between organisms and environments (see reviews by Neale and Kieber,[148] Harrison and Smith.[93])**

3.1 Primary producers

Primary producers such as phytoplankton and macroalgae are dependent on sunlight and are therefore also exposed to UV radiation, which can adversely affect their metabolism.[80] These primary producers take up CO_2 and thus act as a potential sink for CO_2 from and burning of fossil fuels and other anthropogenic CO_2 emissions. Any significant effects of UV radiation on primary producers, most importantly phytoplankton, will, in turn have direct consequences for the global carbon cycle and climate change. Beyond the targets for damage by UV radiation (DNA, lipids, protein) that are common for all biological systems, a major site of damage in primary producers is the photosynthetic machinery. This includes photosystem II and the accessory pigments that funnel light energy to the reaction centers.[88] The subsequent damage will directly reduce primary production. Phycobilin pigments, found in cyanobacteria, cryptomonads, and red algae, are especially sensitive. The extent of the effect of UV radiation shows substantial variation among individual organisms.[80, 242] In nature, the effects are dependent on the level of exposure to UV radiation, but they are

also modulated by temperature[239, 242] and nutrients (section 3.3). Since sensitivity to these effects also varies between species and with environment, exposure to UV radiation has the potential to change the composition of communities. For bottom dwelling primary producers (seagrasses, seaweeds, and small algae), the exposure levels to UV radiation will directly follow the ambient exposure levels, which are a function of incident sunlight and water transparency. For plankton, the same factors are important, but in addition, the mixed layer depth determines the mean level of exposure during the vertical circulation. It also determines the duration of high exposure to UV radiation near the surface. Some phytoplankton produce toxic compounds such as microcystins, and blooms of these algae, called harmful algal blooms (HABs), can have adverse effects on other organisms. While the development of HABs is thought to be mostly a function of nutrient supply, HABs may be modified by exposure to UV radiation.[161]

3.1.1 Inhibition of algal photosynthesis and other processes

Many studies have shown that photosynthesis by phytoplankton and macroalgae is inhibited by near-surface solar radiation, with much of the effect caused by UV radiation.[90, 93] Earlier work focused mostly on freshwater, coastal, and polar systems. More recently, field experiments have shown that inhibition by UV radiation is also important for algal assemblages at lower latitudes and in the open ocean.[8, 79] Exposure to UV radiation also inhibits synthesis of a key organosulfur compound, dimethylsulfoniopropionate, a marine precursor to dimethyl sulfide, a gas that helps ameliorate climate warming through the generation of sulphate aerosols.[8] Laboratory studies continue to investigate how environmental factors affect the response of phytoplankton to UV radiation, and the results of these are discussed in sections 3.2–3.4.

3.2 UV radiation and aquatic primary productivity

A continuing challenge for understanding the importance of the effects of UV radiation on primary productivity of aquatic systems is generalising effects from specific times and locations to the full water column in lakes and over broad oceanic regions. Primary production of the oceans is an important component of the global carbon budget and a critical feedback influencing potential future concentrations of CO_2 in the atmosphere and thus future warming of the climate. This component of the global carbon budget is generally estimated with models, but such models do not currently account for the effects of UV radiation. As a step towards incorporating effects of UV radiation into productivity models, empirical formulas have been developed recently to represent the inhibitory effects of UV radiation on photosynthesis in key species of phytoplankton in the open ocean.[149, 150] Critical to these calculations are biological weighting functions, which provide descriptions of the effectiveness of specific wavelengths of UV radiation for biological processes such as the inhibition of photosynthesis (**Fig. 4**). Biological weighting functions have been estimated for different growth irradiances and temperatures for each key species, thus enabling the scaling of exposure to UV radiation for inhibition of each species' photosynthetic activity over the global ocean (**Fig. 5**). Representative areas of the Pacific Ocean were selected to perform full depth-integrated model estimates of primary productivity. Model estimates that included the effects of full-spectrum UV (UV-B and UV-A) radiation were around 20% lower than when UV radiation effects were omitted.[150] Increased UV-B radiation associated with severe stratospheric ozone depletion had little effect on this estimate (< 2% additional inhibition).[150] This estimate of the additional inhibition due to the increased UV-B radiation

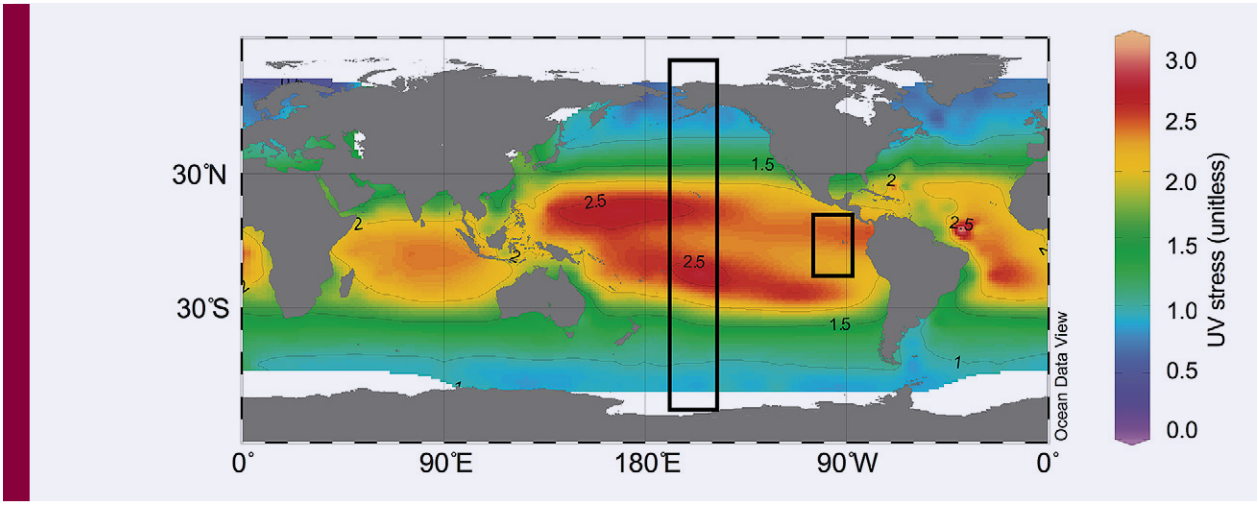

Fig. 5 **Distribution of the intensity of UV radiation stress on photosynthesis for the globally important picophytoplankton, *Prochlorococcus*. The metric for UV radiation stress (colour bar) reflects the combined effect of both incident UV radiation and transparency of the ocean on biologically effective irradiance in the water column (1 = moderate stress). The map shows that the combination of these stress factors is greatest in the subtropical Pacific Ocean. The rectangles delimit areas where the impact of this UV radiation on primary productivity was modeled over the full water column, including the effects of inhibition, which lowered the model estimates of average picophytoplankton production in this region by ~20%. After Neale and Thomas.**[150]

associated with stratospheric ozone depletion is on the low side, but in the same general range (0–6%), as estimates for effects of stratospheric ozone depletion on the productivity of Antarctic and Arctic phytoplankton,[9, 146, 218] as well as Antarctic plants.[154] Further development of these calculations will improve model estimates of open ocean productivity at temperate and tropical latitudes. Global models of primary productivity currently being used have uncertainties that are similar or greater in magnitude than the estimated effect of UV radiation.[187]

In some situations, it is important to consider that exposure of plankton to UV radiation varies greatly on time scales of tens of minutes to hours as water circulates around the surface layer of lakes or oceans (section 2.1). Among the different types of vertical mixing processes, wind-induced Langmuir circulation is particularly important because it is rapid and transports plankton over the full depth of the mixed layer.[147] Thus, phytoplankton can be rapidly (tens of minutes) transported between full exposure at the surface to near darkness at the bottom of the upper mixed layer. In the cold waters of the Antarctic Ocean, UV inhibition and recovery of photosynthesis also occur on scales of tens of minutes to hours.[198] A modeling study compared inhibition of primary productivity in the Ross Sea with and without mixing effects. Inhibition of daily productivity by solar radiation (UV, and PAR, visible light used by plants and algae for photosynthesis), as estimated by the model for conditions during the spring bloom, was about 30% lower with mixing, than without (decreasing from 11% inhibition with no mixing to 7% in its presence).[197] Mixing lessened inhibition because phytoplankton were circulated between the inhibitory near-surface zone and the recovery-promoting irradiance environment of the mid-depth zone. Accurate simulation of Langmuir circulation, however, required a computationally intensive hydrodynamic model, which limits a more general assessment of mixing effects in oceans. Such assessment will be possible if more efficient, yet still realistic methods are developed to simulate vertical transport in the surface layer.

While progress is being made, challenges remain in integrating effects of UV radiation on productivity into modeling frameworks for overall global change. Continuing model development, along with better remote sensing by satellite,[127] will improve the prediction of marine productivity under present and future conditions. This will enhance our understanding of the global consequences of the interaction of UV radiation and other climate change variables including implications for critical marine ecosystem services and food security.

3.3 Effects of UV radiation are modulated by nutrients

Nutrients modulate the adverse impacts of UV radiation on primary producers because UV-protecting pigments and repair of UV-induced damage require nutrients.[17] Some recent research has assessed how increased inputs of nutrients from aerosols affect sensitivity to UV radiation in phytoplankton communities. Deposition of wind-borne dust from the Sahara is an important source of phosphorus to nutrient-limited phytoplankton in the Mediterranean Sea that, depending on the composition of the community, can either augment or diminish the adverse effects of UV radiation.[85] In offshore waters, the adverse effects of UV radiation were accentuated by deposition of this dust, while in nearshore waters, deposition of dust counteracted the adverse effects of UV radiation. Similarly, the composition of species as well as the occurrence of deposition influences the interaction of dust-borne phosphorus and UV responses in lakes[35] and in oligotrophic coastal waters (see section 6.2.1 for southern ocean examples).[34] UV radiation, in combination with additions of phosphorus comparable to those received during a dust event, stimulated the primary producers in a Spanish lake, La Caldera, which receives frequent pulses of dust. This was caused by a trophic shift in mixotrophic plankton (organisms that derive carbon from both photosynthesis and consumption of bacteria) away from grazing (more sensitive to UV radiation) to autotrophy (less sensitive to UV radiation, providing there is enough phosphorus). However; a similar enrichment with phosphorus in another lake, Los Cántaros, in Argentina, produced the opposite result. This community did not have a history of deposition of dust and seemed unable to exploit the increased phosphorus to mitigate effects of UV radiation. However, the trophic shifts of the La Caldera community in response to UV radiation depended on the temporal pattern of dust deposition events. Mixotrophic plankton were less affected by UV radiation in a scenario with a series of smaller dust events *vs* a single large pulse.[31] Phytoplankton from very low nutrient waters in the coastal Mediterranean Sea were affected synergistically or antagonistically by UV radiation and phosphorus.[34] The interactive effects of UV radiation and phosphorus were positive on photosynthesis, but adverse on overall primary production and phytoplankton biomass because the addition of phosphorus allowed the inhibitory effect of UV radiation to be more fully expressed. These studies underscore that changes in sensitivity to UV radiation are related to availability of nutrients, and this is one of the factors mediating how deposition of dust influences community structure of phytoplankton.

Other interactions between nutrients and effects of UV radiation include the increased sensitivity to UV radiation of cyanobacteria grown with a low supply of iron, a critical micronutrient.[128] Cyanobacteria grown with sufficient iron are less affected by UV radiation presumably because iron is a critical component of cellular mechanisms that control concentrations of intra-cellular reactive oxygen species (ROS), and UV-B-induced ROS are known to induce cellular damage. UV-B radiation is also thought to facilitate the uptake of iron by inducing the reduction of Fe(III) in the water to the more bio-available Fe(II).[178]

In contrast, ocean acidification decreases the bioavailability of iron.[195] Inside the cell, greater concentrations of iron will increase the activity of the antioxidant system needed for scavenging ROS. Estimation of the effects of UV radiation on plankton in areas of high iron concentrations can thus underestimate effects of UV radiation when iron is limited, as in many areas of the Pacific Ocean and Southern Ocean.[128] Nitrogen (N) fixation by cyanobacteria is also important in nitrogen-limited oceans, but it is also inhibited by UV radiation in *Trichodesmium erythraeum,* a cyanobacterium that contributes substantially to nitrogen fixation in marine ecosystems.[32]

3.4 Photosynthetic organisms produce protective pigments that reduce the potential for damage from UV radiation

Aquatic primary producers manufacture pigments that protect against UV radiation and function as antioxidants. In higher plants, including aquatic ones, UV radiation can induce the production of anthocyanins[155] (see also Chapter 3). In brown algae, UV radiation induces the production of pigments called phlorotannins, which function as antioxidants[52] and protect against UV radiation.[73] Cyanobacteria, phytoplankton, and macroalgae produce mycosporine-like amino acids (MAAs), chemicals that have a high UV radiation-absorbing capacity and high enough antioxidant capacity that they are used in the cosmetic industry.[91, 121, 143, 168, 217] The diversity of MAAs and the cyanobacteria-specific scytonemins and their biosynthesis pathways were recently described.[174, 194] MAAs accumulated in red algae under increased exposure to UV-B radiation in Patagonia due to springtime stratospheric ozone depletion[144, 145] (**Fig. 6**).

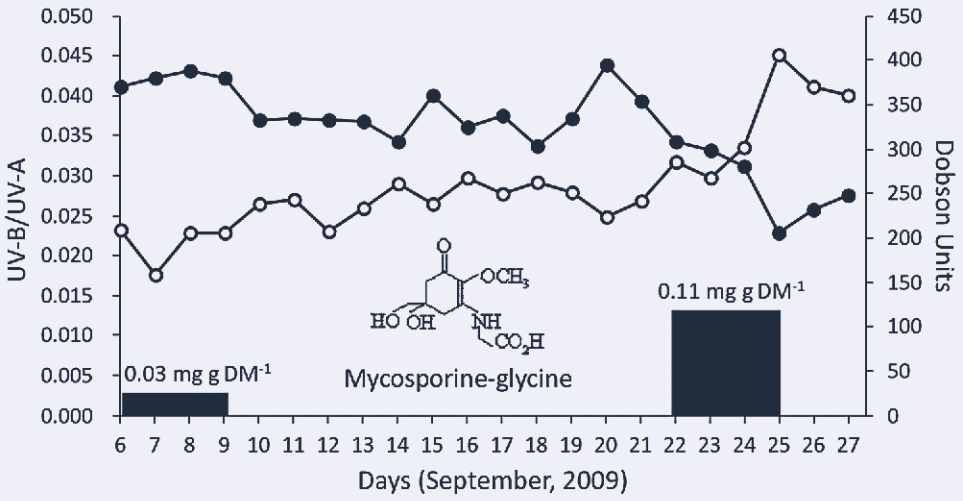

Fig. 6 **UV-B/UV-A ratio of incident radiation (open circles) and stratospheric ozone layer (closed circles) expressed as Dobson units, in Punta Arenas (Chile) in September 2009. In the first period (6 to 9 September), the average UV-B/UV-A was 0.021 and the ozone layer 380 Dobson Units, whereas in the second period (22 to 25 September) the average UV-B/UV-A was 0.035 and the ozone layer 273 Dobson Units. This increase in UV-B radiation due to stratospheric ozone depletion was related to an increase in the average content of mycosporine-glycine (a UV-B-photoprotective compound) in the red macroalga, *Mazaella laminariodes,* from 0.03 ± 0.002 to 0.11 ± 0.008 mg g-1 dry mass (DM) during these two respective time periods. Modified from Navarro *et al.*[144]**

Enhanced MAA content in macroalgae throughout aquatic environments in Brazil has been shown to be related to a high UV radiation, high pH, and high concentrations of phosphate and nitrate.[26]

The broadest surveys to date of MAAs in marine zooplankton and their food resources were performed in the surface waters of an Atlantic Ocean transect (45°S–50°N).[74] They found MAAs in most surface waters but the concentration was highest from the equator to 30°N where it coincided with the occurrence of the nitrogen-fixing cyanobacterium, *Trichodesmium* (**Fig. 7**). Analysis of phytoplankton samples taken during the same survey indicated that *Trichodesmium* was the primary source of the MAAs.[74] Generally there was no correlation between MAAs in zooplankton and MAAs in their food resources in the water, rather the highest MAA content was in zooplankton at higher latitudes.

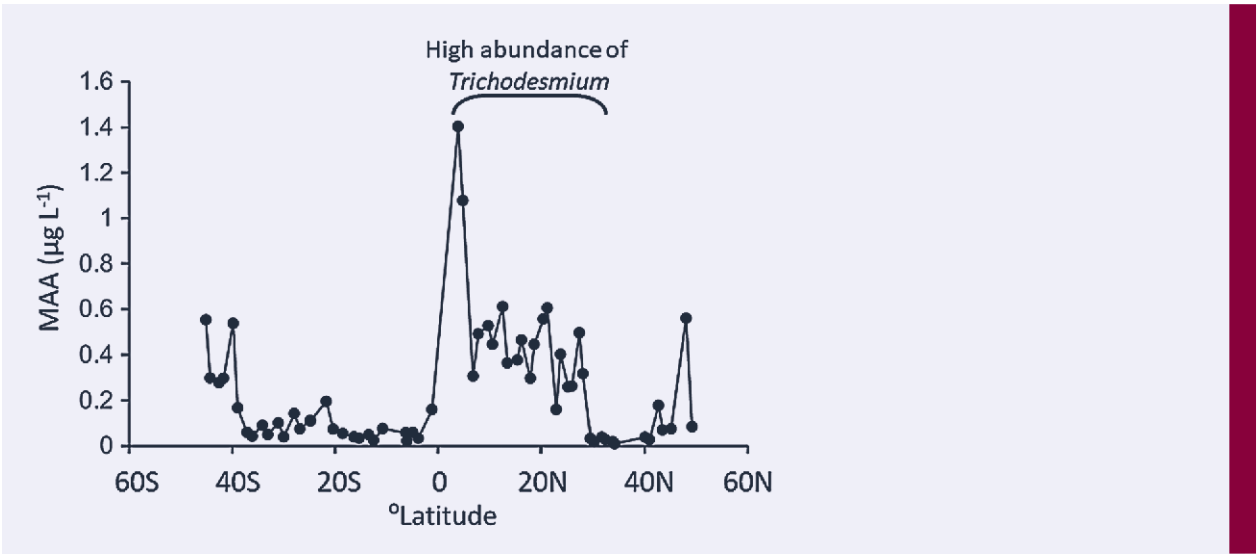

Fig. 7 **Latitudinal distribution of photoprotective compounds (total mycosporine-like amino acids, MAAs) in the Atlantic Ocean, showing a region of high abundance of MAAs at low northern latitudes that coincided with high abundance of the nitrogen-fixing cyanobacterium, *Trichodesmium,* between the equator and 30°N latitude. Modified from Fileman *et al.*[74] with permission.**

3.5 UV radiation and climate change factors can affect seaweed aquaculture and associated ecosystem services

Coastal environments, including natural seaweed communities, provide a range of important ecosystem services such as sequestration of CO_2, provision of food, and supply of useful chemicals for food, cosmetic, and pharmacological industries[30, 117, 181, 208] (see also Chapter 3). Global aquaculture of seaweed has increased nearly three-fold between 2000 and 2014 (from 9.3 to nearly 27 million tonnes) and its value has doubled over this period from about USD 3 billion to USD 6 billion.[66] Production of seaweed in natural and aquaculture systems is affected by environmental conditions including light, temperature, and nutrients.[29, 38, 243] Studies of the effects of UV-B radiation on seaweeds have focused more on early developmental stages than on mature plants.[17] Interactive effects of nutrient supply and UV radiation show

that UV radiation changes macroalgal biomass, community composition, and increases the levels of compounds that protect against UV radiation.[6, 176] Thus, UV radiation combined with other environmental variables can affect the quality of food (i.e., commercial seaweeds, or food and shelter for fish).[6, 17, 23] Corals and calcified algae are potentially more affected by acidification and high solar UV irradiance than non-calcified species; although, in several species, the increase of photosynthetic rate due to increased CO_2 supply can ameliorate the adverse effects of these stressors.[17, 38, 73] The potential for using seaweed aquaculture as a carbon sink and as a strategy for ameliorating increases in anthropogenic emissions of CO_2 has been proposed.[30, 38, 60, 81]

3.6 Evidence continues to accumulate on the adverse effects of UV radiation on zooplankton, fish, and other aquatic animals

Zooplankton are key components in the aquatic food web, transferring energy from primary producers such as algae to fish populations, and controlling algal abundance and overall water quality. Zooplankton also are essential for sustainable fish stocks, but display reduced reproduction, elevated mortality, behavioural changes, and overall reduced fitness when exposed to UV radiation.[3, 42, 92, 104, 159, 173, 225] For example, several species of zooplankton from the Red Sea displayed high sensitivity to solar UV-B radiation,[3] which is striking, since tropical regions are environments with naturally high exposure to UV radiation. Recent laboratory studies also show that UV radiation (340 nm UV-A) can reduce the total number of offspring produced in a common zooplankton species *(Daphnia)* that plays a critical role in freshwater foodwebs.[70] A comparison of lineages from high-UV (high-altitude Bolivia) vs low-UV environments (sea level Swedish lakes) suggests that exposure to UV radiation over an evolutionary time frame has led to Daphnia that are adapted to use an early-life, high-fertility reproduction strategy.[70] The mechanistic pathways whereby UV radiation affects physiology were tested in laboratory studies where zooplankton exposed to artificial UV radiation (peak at 306 nm) allocated more resources to repair of DNA in comparison to controls without UV radiation, leading to reduced growth and reproduction in the UV treatments.[238] While these laboratory experiments can be useful in demonstrating mechanisms of damage by UV radiation and response of the organisms, differences in the spectral composition of UV radiation from artificial lamps *vs* UV radiation in sunlight, preclude extrapolation of these results to nature.

Laboratory experiments with coral reef fish showed that exposure to UV radiation (UV-A, 340 nm) led to elevated respiration and reduced feeding rates.[213] UV radiation (UV-B, 313 nm) also affected swimming performance and metabolic rate adversely in mosquitofish *(Gambusia holbrooki)*, especially at suboptimal temperatures.[112] Furthermore, exposure to UV-radiation (at 313 nm) in adult fish increased the susceptibility to disease among the offspring.[112] However, exposure to UV radiation among parental fish also evoked positive effects such as offspring with higher tolerance to UV radiation as a result of reduced damage to cellular components when young were challenged with UV radiation.[112] The rate of growth and calcification in reef-building corals was also shown to be adversely affected by UV radiation in laboratory experiments (340 nm UV-A) and some of the adverse effects were enhanced by simultaneously increased temperatures.[49]

3.7 Some zooplankton species can detect and behaviourally avoid exposure to high levels of UV radiation in surface waters

Some zooplankton species detect and behaviourally respond to UV radiation.[22, 92, 159, 173] Most species tend to avoid UV radiation by downward or horizontal migration but a few also appear attracted to UV radiation; although the behaviours are species- or even population-specific.[92, 131, 159] The strength of the response is related to size, level of pigmentation, and previous exposure to UV radiation of the organisms.[92, 104, 159] Behavioural responses to exposure to UV radiation are relatively quick, on the order of seconds and minutes (see also Chapter 3 and refs[104, 159, 235]) suggesting that short-term shifts in UV exposure due to changes in cloud cover, sun angle, or other factors, such as UV-absorbing DOM or haze from smoke, can affect the exposure and thus the vertical distribution of zooplankton[92, 212, 235] and their availability as food for fish (see also Chapters 1, 5, and 6) for more on UV radiation and wildfires).

It has been suggested that overall avoidance of surface waters by aquatic organisms is governed by transparency of water, with avoidance of damage by UV radiation dominating in highly transparent waters and avoidance of visual predation in less transparent surface waters.[226] This hypothesis has been evaluated and discussed in several studies.[62, 75, 206] The intensity of UV radiation explained the amplitude of diel (over a 24 h-period) vertical migration in *Daphnia* during a seasonal cycle.[62] Although this field study cannot differentiate between avoidance caused by UV radiation or by other factors positively correlated with UV radiation (e.g., PAR), experimental manipulation of UV radiation in the field has demonstrated the importance of this radiation.[75, 122] Zooplankton tended to avoid surface waters more in lakes with greater exposure to UV radiation than in those with less exposure.[75, 206] Vertical distribution of zooplankton also shifted in a lake where transparency varied over time.[75]

3.8 Zooplankton, fish, and other animals have physiological adaptations to reduce potential damage from UV radiation

Evidence continues to accumulate that, apart from avoidance behavoiur, zooplankton have several other defense mechanisms to prevent excessive damage by UV radiation. The UV-exposure in Arctic waters is rapidly increasing due to reduced sea-ice (see section 2.1), with consequences for zooplankton and their ecosystem services. For example, the copepod zooplankton genus, *Calanus,* is essential in supporting the North Atlantic Ocean and Arctic Ocean fisheries.[25, 219] *Calanus* species in the Arctic generally over-winter in deep water and ascend to shallow waters during spring to feed on algae that grow in the spring-early summer. It was shown that *Calanus* accumulate UV-protective compounds such as MAAs from their algal diet in synchrony with ice-out.[107] This suggests an efficient UV-protection among *Calanus,* but it is not known if this adaptation will remain effective if ice-out, and hence exposure to elevated UV radiation, come earlier in the season.

Accumulation of carotenoids, such as astaxanthin, is another adaptation among zooplankton to avoid damage from UV radiation. These substances are accumulated by copepod zooplankton when exposed to UV radiation (artificial 340 nm UV-A).[28] However, these substances may also accumulate for other purposes and do not necessarily indicate a

response to UV radiation. For example, carotenoids can be coupled to fatty acid metabolism during winter when UV radiation is absent or very low.[191] Furthermore, concentrations of carotenoids in Arctic *Calanus* were not correlated with levels of UV exposure.[107] On the other hand, the highest carotenoid levels may occur concurrently with abundant UV-protective MAAs.[204] Hence, the role of carotenoids as UV-protective compounds is uncertain. Either way, carotenoids are strong antioxidants and are believed to have several beneficial functions in organisms exposed to UV radiation.

Other important zooplankton, such as the cladoceran *Daphnia* spp., have elevated melanin concentrations in their outer shell to avoid damage by UV radiation.[97, 100] Melanin found in lake sediments has been measured to estimate historic UV radiation exposure coupled to environmental change (see Chapter 3 for details on other paleoproxies).[152, 153] Aquatic insects such as damselflies also accumulate melanin upon exposure to UV radiation (UV-A, 340 nm), but at a cost of delayed metamorphosis to the adult stage and a smaller body size[55] suggesting fitness costs associated with exposure to UV radiation. When exposed to solar UV radiation, amphipods (crustaceans) accumulated photoprotective compounds (determined by absorbance peaks of extracts between 310–360 nm) from their diet of seaweed.[214]

Further adaptations to avoid UV-induced damage were studied by Connelly *et al.*[42] demonstrating that *Daphnia* supplied with vitamin D3 survived better under laboratory exposure to UV-A radiation (340 nm) than controls without UV-A, but the mechanism for this positive effect is not known. Some zooplankton, such as copepods, can also defend themselves against UV radiation by inducing heat shock proteins. These proteins reduce cellular damage by stabilising proteins during seasons of high exposure to UV radiation.[204]

3.9 Reactive oxygen species produced by UV-DOM interactions have localised impacts

UV radiation damages DNA and other cellular structures directly, but it can also indirectly cause damage via the production of ROS, which in turn damage the same cellular constituents. The production of ROS is increased when DOM is exposed to UV radiation.[234] The concentrations of DOM have been increasing in recent years in many lakes and coastal zones (section 2.1), which is likely altering the depth distribution of ROS production. It has been demonstrated that ROS can damage DNA in *Daphnia,* and reduce bacterial and some phytoplankton production.[12, 125, 234] Laboratory studies with 340 nm UV-A lamps have implicated ROS in the possible inhibition of uptake of dietary nutrients in *Daphnia.*[237] However, recent models suggest that damaging concentrations of photoproduced ROS, in the form of hydrogen peroxide, likely occur only in the top few centimeters of most lakes.[236] Additionally, ROS break down very rapidly. Thus, long-term damaging ROS exposure is unlikely in nature due to wind-driven mixing of the water column and the high attenuation of UV radiation in systems with elevated DOM concentrations (**Fig. 3**). For example, field measurements of aquatic insect larvae *(Chaoborus)* showed 50 times lower damage of DNA in insects from a high DOM pond compared to those in a low DOM pond.[129] Overall, these data suggest that UV-shading by DOM outweighs the elevated ROS production due to increased DOM concentrations, reducing net damage to aquatic organisms (see also section 2.1). Some potential exceptions where ROS may be more important are in very shallow systems, in surface waters during periods of no wind, or via biological production during intense phytoplankton blooms.[46, 215, 247]

3.10 UV radiation can affect interactions among species and composition of communities

Few studies examine the effects of UV radiation on multiple trophic levels at the same time, taking into account trophic interactions and differential tolerance to UV radiation among species. The susceptibility to UV radiation is species-specific and may be important in structuring the composition of zooplankton communities.[135, 228] Field surveys of zooplankton communities suggest shifts in species composition with changing exposure to UV radiation.[135] However, incubation of zooplankton communities in different UV radiation environments for several months suggests that UV radiation has only minor effects on overall community composition, and field patterns could also be explained by coincidental changes in other factors such as temperature.[105, 135]

Although a recent meta-analysis suggests that the adverse effects of UV radiation are, on average, equally damaging to all trophic levels,[163] this is not always the case. Evidence shows that changes in UV radiation can alter species interactions and community composition in aquatic ecosystems, and that climate change may be indirectly causing these changes in exposure to UV radiation. For example, a common predatory insect larva, the phantom midge *(Chaoborus nyblaei)*, is relatively sensitive to UV radiation, in part because it has a transparent body. Recent research shows that this predator appears to be increasing its range among shallow alpine ponds where UV-absorbing concentrations of DOM are high.[129] Concurrent with the spread of this midge, their prey, the relatively more UV-tolerant fairy shrimp *(Branchinecta paludosa)*, is being reduced.

Changes in the UV radiation environment will occur in response to changes in absolute radiation but are even more likely via climate-induced changes in the amount of UV-absorbing substances (e.g., DOM) in the water column (section 2.1). For example, in situ experiments in mesocosms (large enclosures placed in a lake) that simulated the inflow of DOM revealed that DOM stimulates the microbial food web by providing nutrients, while reducing the damaging exposure to UV radiation,[190] as well as leading to shifts in the structure of the zooplankton community through both direct and indirect effects on UV radiation.[44] Shifts in the overall species composition in response to UV radiation are most likely limited to highly transparent and/or very shallow aquatic ecosystems due to the high UV-absorbing capacity of DOM.

4 UV radiation provides valuable aquatic ecosystem services that are being compromised by reductions in water clarity

In recent decades, stratospheric ozone depletion has led to widespread concerns regarding the adverse effects of elevated exposure to short wavelength UV-B radiation. There are, however, some beneficial effects of UV radiation that will be compromised due to both the recovery from stratospheric ozone depletion and the acceleration of climate change. For example, just as solar disinfection (SODIS) is used to purify drinking water in plastic bottles, and artificial UV radiation is used to disinfect drinking water in municipal supplies such as New York City, NY, and Cincinnati, OH, USA, the UV radiation in sunlight can disinfect surface waters of parasites and pathogens, thus reducing the transmission of waterborne diseases (see also Chapter 5). Many human pathogens as well as pathogens of aquatic organisms

are inactivated by exposure to UV radiation, and even by short wavelength PAR in solar radiation.[158, 227] This valuable ecosystem service is threatened by increasing concentrations of DOM, because DOM selectively absorbs the most powerfully disinfecting short wavelength UV-B (**Fig. 4**). Modeling the potential for UV inactivation has shown that surface waters with higher concentrations of DOM can reduce the solar disinfection potential of the solar UV-B radiation by tenfold or more.[227] In regions where water transparency has declined, reductions in underwater exposure to UV radiation may thus threaten global health and contribute to the spread of infectious diseases. One important caveat here is that some pathogens may be inactivated by ROS produced by the indirect effects of UV radiation on DOM (section 3.9 above and section 5.1 in Chapter 5 and related discussion). In some cases, increases in DOM may not reduce solar disinfection and may even increase it for pathogens that are more sensitive to inactivation by ROS than to direct DNA damage (see Chapter 5).

Climate change is altering exposure to UV-A as well as UV-B radiation in aquatic ecosystems through changes in ice cover, increases in DOM, and reductions in the depth of mixing of the surface waters (section 2.1). UV-A radiation has beneficial effects that include contributing to photoenzymatic repair of UV-B-damaged DNA.[175] UV-A radiation is also important in orientation and foraging in many aquatic organisms such as fish and zooplankton that have UV-A photoreceptors. Foraging rates were higher for freshwater largemouth bass in the presence of UV radiation (< 400 nm) than when it was absent under natural field conditions.[123] Similarly the importance of UV radiation for foraging success has been demonstrated in zebrafish in the laboratory, by comparing mutants with few UV receptors (cone cells) to normal zebrafish with abundant UV cone cells.[76] In contrast, laboratory experiments with bluegill sunfish[124] show no evidence of UV-enhanced foraging, and laboratory experiments with a reef fish show that UV radiation from artificial lamps (< 400 nm) can actually reduce foraging success.[213] A potentially important interaction is that, at higher concentrations, DOM may reduce the visual field (reactive distance) of fish in addition to reducing the penetration of UV radiation. Thus, depending on the fish species and optical conditions, UV radiation may either enhance or inhibit foraging. These differences may be species-specific or vary due to differences in either the intensity or the spectral composition (wavelengths) in natural *vs* artificial sources of UV radiation. Regardless of the effects of UV-A radiation on foraging, the ability to detect and avoid UV-A radiation has the potential to allow aquatic animals, including small, transparent, young fish in their first year of development, to avoid more damaging UV-B that does not penetrate as deeply in the water column as UV-A radiation. This ability of aquatic organisms to avoid damage by UV radiation has the potential to increase survival rates and year class strength of both recreationally and commercially valuable fish species.

Another beneficial effect of solar UV radiation lies in the photo-degradation of DOM, which provides a source of more bioavailable fixed carbon and nutrients that can stimulate aquatic food webs. Photo-degradation has been demonstrated to be particularly important in Arctic surface waters, which are receiving DOM released into runoff water from thawing permafrost.[48] This is, however, a double-edged sword. While photo-degradation has the potential to stimulate ecosystem productivity, it also releases greenhouse gases through the conversion to a bioavailable form of terrestrially-derived fixed carbon that has been locked up in permafrost for millennia or longer, thus aggravating climate warming (see Chapter 5).

5 UV effects are highly dependent upon interactions with other aspects of environmental change

5.1 Acidification of oceans changes responses of aquatic organisms to UV radiation

Increasing amounts of CO_2 in the atmosphere due to human activities result in higher concentrations of CO_2 in open oceans, but the net changes in the water depend on the mixing dynamics. The oceans are a major sink for anthropogenic emissions of CO_2.[188] CO_2 reacts with water to produce carbonic acid, which dissociates into a carbonate ion and two protons, thereby decreasing the pH. This acidification has adverse effects on some aquatic organisms and their protection from damage by UV radiation, as described in more detail below.

A 30% increase in protons results in a reduction of pH by 0.1 units, and acidification of oceans is predicted to reduce the pH by 0.3–0.4 units by year 2100 under a business-as-usual scenario (RCP8.5).[82] Some inland reservoirs and larger lakes are either already showing, or expected to show decreases in pH similar to those observed in the oceans.[164, 221] In contrast, however, the recovery of many inland waters from acid deposition (e.g., acid rain), has increased the pH of some inland waters by up to a full pH unit in regions of Europe and North America.[140, 230] The close proximity of human activity to lakes, and the larger ratio of catchment area:water surface area of most lakes *vs* oceans, suggest that future changes in the pH of oceans will be affected by atmospheric CO_2, while the pH of inland waters such as lakes and reservoirs will be more sensitive to other factors related to climate change and land use.

Acidification of oceans alters water chemistry, affecting primary producers differently depending on latitude and other environmental drivers such as solar UV radiation, temperature, nutrients, and concentrations of CO_2.[27, 90, 171, 177] Some harmful algal species have a low sensitivity to solar UV radiation and, consequently, increasing exposure to UV radiation favours them, resulting in more harmful algae. These shifts may be increased by higher temperatures and nutrients.[157] The interacting effects of ocean acidification and higher temperatures can also stimulate the synthesis of toxic substances, as found for one harmful algal species.[94]

Many phytoplankton, macroalgae, and animals produce calcified exo- or endo-skeletons that are thought to have several functions, including protection against predators and solar UV radiation.[139] For photosynthesising organisms this requires about a third of the cell's photosynthetic energy. However, this strategy has been successful as indicated by the wide distribution and biomass production of ecologically important organisms such as calcifying algae (e.g., coccolithophorids). Ocean acidification reduces calcification in aquatic organisms, potentially exposing them to increased solar UV radiation.[87, 177, 207] Because of the different reactions of particular species or populations to decreasing pH, interactions between UV radiation and ocean acidification may produce shifts in biodiversity and community structure, affecting grazers and fisheries.[86]

5.2 UV radiation interacts with artificial sunscreens, plastics, and other pollutants with adverse effects on aquatic ecosystems

UV radiation interacts with a wide range of pollutants in aquatic ecosystems (see also Chapter 5). In some cases, UV radiation enhances the potential toxicity of pollutants via photochemical reactions. In most cases, UV radiation degrades and removes pollutants, changing their chemical composition and sometimes making them less harmful. For example, mercury is a key contaminant in many freshwaters. The toxicity and transport of mercury up the food web to fish occurs through uptake of methylmercury. UV-B radiation dominates the photo-demethylation process,[84] and the fraction that is photo-demethylated varies between 25% to 80% depending on water transparency.[166] Exposure to UV-B radiation thus reduces the uptake of mercury to fish. Exposure to UV radiation can also increase the toxicity of contaminants such as some pesticides and polycyclic aromatic hydrocarbons (PAHs) to aquatic organisms such as fish and amphibians.[4, 5, 244] Some pollutants can negatively affect the ability of aquatic organisms to detect and respond to damaging solar UV radiation. For example, amphibian tadpoles that normally behaviourally avoid damaging solar UV radiation do not avoid it when exposed to the pesticide endosulfan which was widely used in the past.[245]

Two emerging pollutants of concern that interact with solar UV radiation include sunscreen compounds and microplastics (plastic particles < 5 mm diameter). Sunscreen compounds are chemicals that absorb or reflect solar UV radiation and are commonly classified as either organic (e.g., oxybenzone) or inorganic (TiO_2 or ZnO). Carbon-based and inorganic sunscreens can be toxic to aquatic organisms, and can impair the development of corals,[59, 209] sea urchins,[45] and fish,[77] as well as affect gene expression[160] and development in bottom-dwelling freshwater insect embryos and larvae.[33] These compounds are widely used in a variety of personal care products and have demonstrated benefits for human health and protection against the damaging effects of UV radiation (see Chapter 2). However, these compounds and their metabolites are found in many aquatic ecosystems and researchers are just beginning to identify and understand their environmental effects. Highlighting the growing public awareness of potential adverse ecological effects, the US State of Hawaii recently passed a bill, which will go into effect in 2021. The bill bans the sale and distribution of sunscreens containing oxybenzone and octinoxate due to their negative environmental impacts, especially on corals.[192] Other legislation has been submitted to the European Union that calls for a ban on oxybenzone-containing sunscreens.[224] MAAs found in phytoplankton and macroalgae (section 4.3.6) serve as natural UV sunscreens, and may have potential as alternative sunscreens for humans[37, 121] (see also Chapter 2).

UV sunscreen compounds have been found in freshwater, coastal, and marine ecosystems in many different regions and countries.[11, 170, 210] Environmental concentrations of UV sunscreen compounds can vary widely,[110, 189, 210] with nearby population density being an important predictor of environmental concentration.[241] Concentrations can be especially high near swimming beaches and waste-water discharge sites,[170, 210] but detectable concentrations are also found in remote areas such as the Arctic.[210]

One challenge is that not all studies of potential impacts are conducted at ecologically realistic concentrations.[186] Despite these limitations, recent studies highlight the ways in which sunscreen compounds might impact aquatic food webs and exacerbate other regional

or global environmental problems. For example, sunscreens can cause bleaching of coral and death, even at concentrations found in nature, and at least 10% of reefs might be sensitive to such impacts.[53, 209]

The main mode of action of sunscreens on corals appears to be induced oxidative damage, which is enhanced when the compounds are exposed to solar radiation.[59, 193] A few studies indicate that certain organic sunscreens may also be endocrine disrupters.[114, 119] Some organic sunscreens are known to bioaccumulate in the muscle and lipids of organisms.[111] Adverse effects of organic sunscreens have been identified across a wide range of aquatic taxa such as phytoplankton, protozoa, crustaceans, and fish.[59, 110, 189] Common inorganic sunscreens such as TiO_2 and ZnO nanoparticles have been found to inhibit the growth and photosynthesis of marine phytoplankton,[138, 202] as well as decreasing the survival and reproduction of grazing zooplankton,[108] and, therefore, may adversely impact fisheries. Because species have differential sensitivities to these commercial UV-absorbing compounds, sunscreens may shift the relative species composition in affected aquatic ecosystems.[189, 193] However, because adverse impacts vary across taxa, predicting the net effects on ecosystems is difficult.

In addition to some sunscreens, UV radiation may exacerbate the environmental impact of other pollutants such as plastics. On the order of 5 to 10 megatons of plastics are dumped or washed into the oceans each year. Exposure of larger plastic pieces to UV radiation and consequent photo-oxidation is the most important process initiating the formation of microplastics in the marine environment[7, 83] (see also Chapter 7). The relative costs and benefits of degradation of plastics by UV radiation are still unknown in terms of food security and ecotoxicological consequences. Surveys have revealed that about 20% of marine fish in seafood markets contain microplastics, creating a potentially emerging threat to food security.[211] The impact of potential exposure to UV radiation on the degradation and fate of plastics in aquatic ecosystems depends on whether they float or sink, because this will determine the levels of UV radiation to which they are exposed, and thus the rate of photo-degradation. Higher density plastics such as polyvinyl chloride (PVC) and polyethylene terephthalate (PET) sink to the bottom where low exposure to solar UV radiation reduces photo-degradation.[7] Substantial amounts of buoyant plastics float in surface waters where they are transported worldwide, with extensive pollution even in remote oceans and beaches. Plastics degrade very slowly and can persist in natural environments for decades.[7] However, only about 1–10% of the plastics dumped into oceans annually remain in the surface waters.[39] Thus there is an open question about the overall importance of solar UV radiation in contributing to the breakup and decay of plastics, or how much changing levels of UV radiation alter the cycling of plastics in the global oceans.

Exposure to high levels of solar UV radiation can degrade plastics into smaller microplastic particles (< 5 mm, **Fig. 8**) or even smaller nanoplastics (20–1000 nm; see also Chapter 7). The primary concerns about microplastics are (1) that they are contaminants that may be toxic to plankton, the fish that ingest them,[15] and potentially humans, and (2) the presence of positively buoyant microplastics may slow the sinking of organic carbon to oceanic depths, thus decreasing carbon sequestration in the deeper ocean layers.[40] Microplastics are ingested by zooplankton and may settle out to the bottom of lakes and oceans in their fecal pellets, or be transferred to higher trophic levels including fish.[7, 39] Copepods (small crustaceans) are the most abundant zooplankton grazers in the world's oceans and a key link in oceanic food webs. Both copepods and some fish that feed on copepods are important in the biological pump that transfers organic carbon to the deep ocean by vertical migration or settling of fecal pellets. On the order of 73% of mesopelagic fish examined from a warm-core eddy in the

Fig. 8 **Plastics are a pervasive pollutant in marine ecosystems, as seen here on Whitsand Beach, Cornwall, UK (left). Both UV radiation and aquatic biota play a critical role in the creation, fate, and toxicity of plastics. UV radiation is the primary environmental factor creating smaller microplastics that are ingested by copepods, the most abundant grazers in the oceans of the world. Copepods can in turn serve as a conduit to fish and other seafood consumed by humans; or their fecal pellets, which may contain microplastics (right, with fluorescent microplastics shown for visibility), can contribute to the sedimentation of these plastics to deeper oceanic environments. Photographs by Dr Matthew Cole. Right photo from Clark *et al.*[39] with permission.**

Northwest Atlantic contained microplastics.[223] Although not as well-studied as microplastics in the oceans, initial studies indicate that microplastics are as prevalent in many freshwater ecosystems on several continents as they are in the oceans.[61] Nanoplastics in the 50 nm size range have been shown to be ingested by the common freshwater zooplankton *Daphnia,* and transferred to fish through the food web where they in turn accumulate in the brains of fish and can alter their feeding behaviour.[136] This study used manufactured polystyrene particles, and it is unknown whether these particles respond similarly to nanoplastics found in the environment. *In vitro* studies with human cells have shown cytotoxic effects of micro- and nanoplastics, as well as the ability of particles less than 10 μm to carry toxic metals such as mercury and also cross the blood-brain and placental barriers.[14] However, our knowledge of the role of microplastics and nanoplastics is in its infancy, and more information is needed on the extent to which they may serve as a conduit of plastics and other toxins to the seafood supply of the world's markets, potentially threatening human health and food security.[14, 240]

6 Effects of stratospheric ozone depletion on climate and aquatic ecosystems in the southern hemisphere

In addition to its direct effects on incident UV-B radiation, stratospheric ozone depletion has resulted in major changes in southern hemisphere climate, affecting atmospheric and oceanic circulation (see also Chapter 3), with consequent effects on aquatic ecosystems. The changes in climate are captured by the Southern Annular Mode (SAM, an index of atmospheric variability, which equates to the difference in mean sea level pressure between 60°S and 45°S). Increasing greenhouse gases and ozone depletion over Antarctica have both pushed the SAM towards a more positive phase (greater latitudinal difference in pressure), and the SAM index is now at its highest level in at least 1000 years.[2] Section 2.1.4 discussed how the trend towards a more positive phase of the shifts in SAM have latitude-specific effects on exposure to UV radiation. The following section considers additional climatic effects other than exposure to UV radiation.

6.1 Changes to oceanic circulation

The increasingly positive SAM is manifest in a poleward shift and/or strengthening of the mid-latitude surface wind, which, in turn, plays a fundamental role in ocean circulation. In general, the prevailing westerly wind in the middle latitudes acts to drive northward transport in the underlying ocean (**Fig. 9**). This creates a region of upwelling on the poleward side (around 60°S), and surface transport towards the equator into the sub-Antarctic zone (between middle latitudes and subtropical zones)[179] (**Fig. 9**, see also Chapter 3). This circulation is intensified and shifted south during the positive phase of the SAM, which models suggest is due to the combined effects of stratospheric ozone depletion over Antarctica and climate change. For the austral summer, modelled trends in the vertical ocean circulation are mainly attributable to stratospheric ozone depletion.[199] Depletion of ozone was found to be responsible for the subsurface cooling north of 35°S (i.e., transition between the sub-Antarctic and subtropical zones), with increasing greenhouse gases as the main driver of warming at higher latitudes.[199] In conjunction with warming, the Southern Ocean has largely become fresher (less salty) which is attributed to increased precipitation and runoff.[199]

The most recent scientific assessment of stratospheric ozone depletion[233] concludes that there is evidence for large effects of stratospheric ozone depletion on Southern Ocean atmospheric and oceanic circulation, temperature, and salinity. However, some modelling studies suggest that the contribution of the ozone 'hole' to warming and freshening of the Southern Ocean water is smaller than that of greenhouse gases (likely on the order of 30% or less). Changes in circulation also affect sea-ice extent and duration (for details see Chapter 1); however, the role of stratospheric ozone depletion in recent trends of Antarctic sea-ice remains a highly debated topic[233] (Chapter 1).

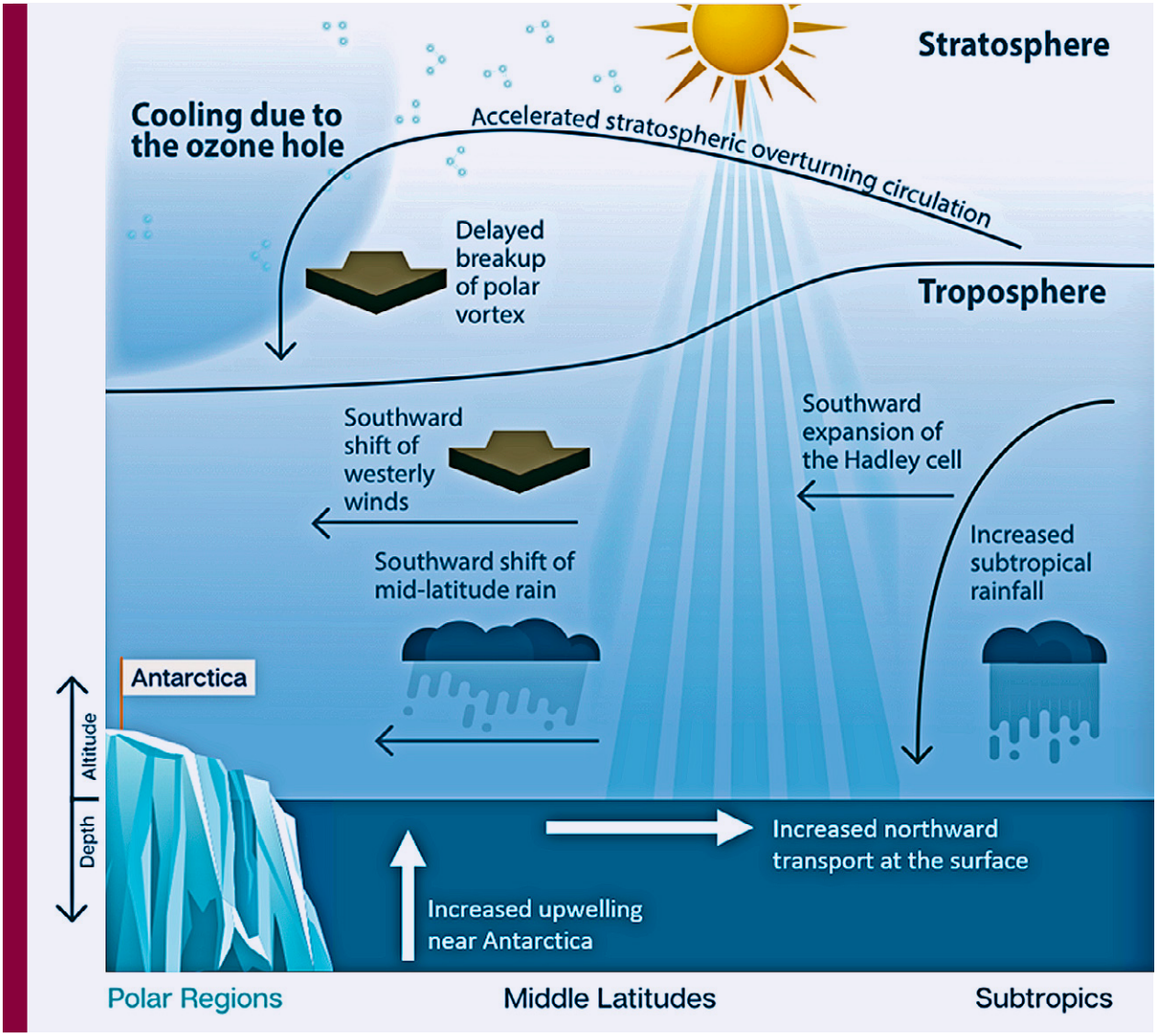

Fig. 9 **Cross-section showing the effects of depletion of ozone on circulation in the Southern Ocean. See text for details.**

6.2 Ecosystem and population impacts from changes in atmospheric and oceanic circulation associated with stratospheric ozone depletion and the positive Southern Annular Mode

6.2.1 Changes to ocean carbon uptake

The Southern Ocean plays a very important role in the global carbon budget by absorbing $CO_2$from the atmosphere and sequestering it in the deep ocean, thus reducing the rate at which CO_2 is increasing in the atmosphere.[120] The positive SAM phase reduces net oceanic uptake of CO_2 from the atmosphere and the ocean's ability to sequester it in the deep ocean by altering large-scale ocean circulation.[64, 120, 179] Partly, this is due to the upwelling of deep water that already has high amounts of CO_2 and cannot absorb more. Additionally, the positive SAM phase affects primary productivity through changes in light and nutrients, some the consequences of which are illustrated in **Fig. 2** (see also Deppeler and Davison[58]). These, in turn, alter how much CO_2 phytoplankton can absorb from surface waters and sequester as organic carbon. The direction of these changes differs by latitude as does the overall effect on productivity, so the net outcome of the positive SAM phase on the ocean biological uptake of CO_2 is variable. In the sub-Antarctic zone, long-term warming and a shallower mixed layer depth are believed to reduce primary productivity by reducing transport of nutrients from deep waters into the surface layer, despite higher availability of PAR (**Fig. 2**, top panel). However, where the main limiting nutrient, iron, is available, (e.g., in the South Atlantic), increased exposure to PAR can increase primary productivity. Stronger winds and drier conditions associated with positive SAM can also enhance iron concentrations in the ocean by transporting more dust to the ocean from terrestrial sources, such as South America (**Fig. 10**, **Table 1**).[64, 179, 232] Consistent with this, there has been a long-term trend of increasing phytoplankton biomass in the South Atlantic sector of the sub-Antarctic zone, but decreasing biomass in other areas lacking iron inputs.[126]

At about 60°S latitude, increased wind speeds are deepening the mixed layer depth, reducing light, and increasing upwelling and iron availability (**Fig. 2**, bottom panel). Models differ as to whether the long-term outcome of these increased wind speeds will be an increase or a decrease in productivity[58] and the empirical data are limited. A comparison of observed trends with predictions using a model (CMIP5, Coupled Model Intercomparison Project 5), based on the IPCC scenario RCP8.5, suggested that phytoplankton biomass has been decreasing in the latitudinal band between 50° and 60°S.[126]

Long-term decreases in duration and extent of sea-ice are expected due to the combined effects of global warming and the positive SAM phase. In addition to the effects of warming temperatures, increased ocean upwelling erodes the bottom of sea-ice, which results in substantial declines in sea-ice around the Antarctic Peninsula. However, in the short-term, northward transport is extending the sea-ice zone where upwelling is weaker, for example, in the Ross Sea.[58] Where sea-ice has been decreasing, phytoplankton biomass has increased at the expense of sea-ice algae.[58, 126] The main ecosystem impact of changes in sea-ice may be through changes in the timing and composition of primary production, which controls other ecosystem aspects such as fisheries, birds, and mammal populations in both marine and freshwater ecosystems (see **Table 1**).

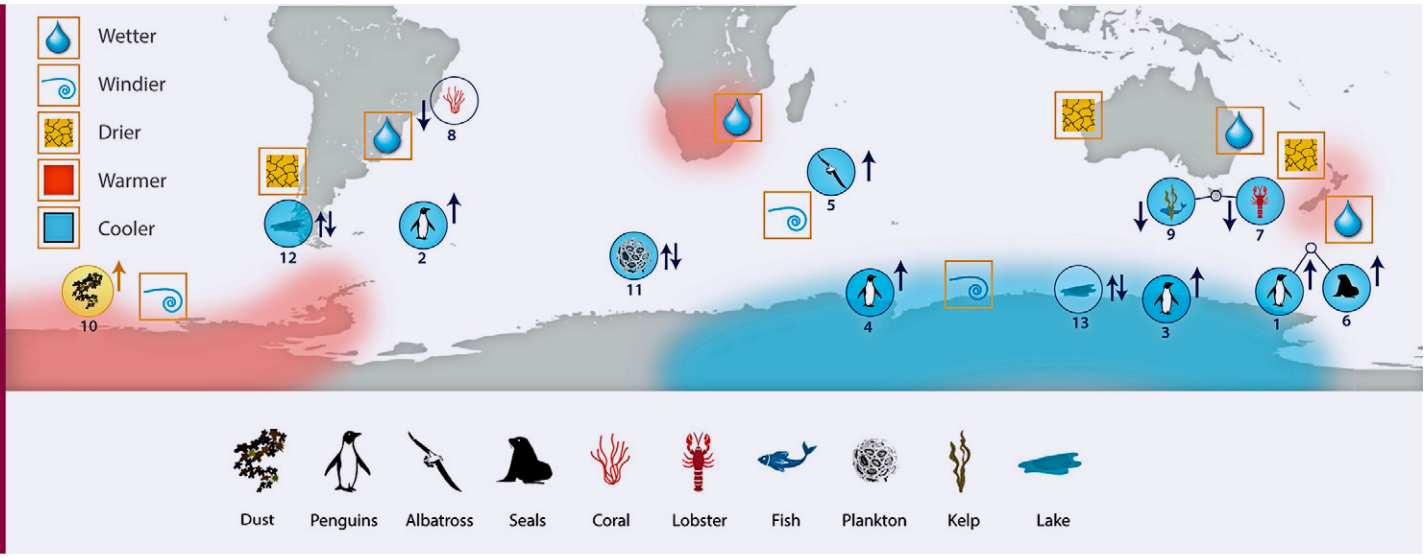

Fig. 10 **Map of the southern hemisphere showing how stratospheric ozone depletion affects the climate and environment, and the effects of these abiotic changes on marine ecosystems and populations. Symbols show types of organism, ecosystem or entity affected (see key), with numbers referring to Table 1, which provides location and species details. Arrows indicate direction of effects on biodiversity, up = positive; down = negative effects; two-way arrows indicate changed biodiversity.**

Table 1 **Summary of how climate change, driven by stratospheric ozone depletion, affects marine ecosystems and populations across the southern hemisphere. Locations (see Fig. 10) and references are provided.**

Type of ecosystem or organism affected (marker number Fig. 10)	Species details and biological effects	Location	References
Marine animals			
1	Royal penguins *(Eudyptes schlegeli)*; early egg laying	Macquarie Island	Ref.[101]
2	Rockhopper penguins *(Eudyptes chrysocome chrysocome)*; positive effects on body mass and reproductive investment in females	Falkland Islands/ Islas Malvinas	Refs[56, 57]
3	Emperor penguin *(Aptenodytes forsteri)*; juveniles show increased survival	Dumont D'Durville	Ref.[1]
4	Adélie penguins *(Pygoscelis adeliae)*; earlier egg laying	Mawson	Ref.[63]
5	Wandering Albatross *(Diomedea exulans)*; increased female body mass and better reproductive outcomes	Crozet islands	Refs[67, 68, 220]
6	Elephant seals *(Mirounga leonine)*; increased maternal body size	Macquarie Island	Ref.[137]

Type of ecosystem or organism affected (marker number Fig. 10)	Species details and biological effects	Location	References
7	Eastern rock lobsters *(Sagmariasus verreauxi)*; distributions shifted south	Tasmania	Ref.[36]
Ocean ecosystems			
8	Corals; declining growth rates	Brazilian coast	Ref.[65]
9	Declines in giant kelp bed extent and fish distributions linked to changing ocean currents	Eastern Tasmania	Ref.[109]
10	Increased transport of dust results in iron fertilisation and could increase productivity of plankton	Southern Ocean	Ref.[64]
11	Changes to the mixed layer depth affect the distribution of both zoo- and phytoplankton, with subsequent consequences for their exposure to UV radiation	Southern Ocean	Ref.[58]
Lake ecosystems			
12	Changes in lake fauna	Eastern side of the Andes	Ref.[50]
13	Lakes becoming more saline causing biodiversity changes	East Antarctic	Ref.[102]

6.2.2 Seabirds, marine mammals, and marine ecosystems

Together with climate change, the effects of stratospheric ozone depletion on Southern Ocean climate can have diverse and substantial consequences for populations of foraging sea birds and seals (**Fig. 10**, **Table 1**).[21, 67, 220] In the sub-Antarctic, the average weight of female wandering albatross is positively associated with the SAM phase, while the age at reproduction is negatively related with the SAM phase. This has led to improved breeding success in recent decades.[67, 220] The increasingly positive phase of SAM is also associated with better outcomes for some marine mammals on sub-Antarctic islands. For example, weight of southern elephant seals on Macquarie Island is positively associated with the SAM phase and negatively with the extent of sea-ice.[137]

Across the southern hemisphere, breeding success for four different penguin species (**Fig. 10, Table 1**) rose with the increasing positive SAM phase.[56, 57, 63, 101] Some of these species, such as the Southern rockhopper penguins *(Eudyptes chrysocome chrysocome)*, have 'vulnerable' conservation status.[56, 57] Improvements in breeding success are associated with greater weight of adult Southern rockhopper penguins in the sub-Antarctic,[57] and earlier start-date of egg-laying in Royal penguins.[101] In the sea-ice zone near the Antarctic continent, the positive SAM phase is associated with a greater weight of juvenile Emperor penguins and earlier egg-laying date for Adélie penguins.[1, 63] These improvements in penguin populations are likely driven by increases in their food supplies in the latitude bands they inhabit, and imply that, by altering the climate, stratospheric ozone depletion results in beneficial effects on some

populations of marine birds in certain regions of the Southern Ocean. However, as discussed previously, positive and negative effects of the positive SAM phase on oceanic productivity are likely, and it is not currently known how bird and mammal populations are changing in those areas where productivity is declining (**Fig. 10**).

Changes in stratospheric ozone depletion and its consequent effects on circulation in oceans could also be altering the distributions of other marine species. For example, recent intensification of the East Australia Current, associated with the positive SAM phase, has shifted the population range of the Eastern rock lobster *(Sagmariasus verreauxi)* southward by ca 270 km.[36] Related to the positive SAM phase, the predicted incursions of warm, nutrient-poor water from the East Australia Current along eastern Tasmania have also increased in strength, duration, and frequency.[109] This has likely contributed to regional declines in the extent of giant kelp beds, as well as to marked changes in the distribution of near-shore fish and octopus, and allowed northern warmer-water species to colonise Tasmanian coastal waters.[109, 169] Declines in growth rates in Brazilian corals since the 1970s have also been linked to increasing sea surface temperatures, which were correlated with stratospheric ozone depletion over Antarctica.[65] These findings indicate that there are widespread and far-reaching effects of climate change driven by stratospheric ozone-depletion on marine[1] as well as terrestrial[180] (see also Chapter 3) ecosystems across the southern hemisphere.[162]

7 Knowledge Gaps

Although great advances have been made in recent years in our understanding of the interactive effects of UV radiation and changes in climate and other environmental factors on aquatic ecosystems, major knowledge gaps still exist. Here we assess the most critical remaining knowledge gaps. One of the overarching knowledge gaps is the lack of good data on the spectral dependence of UV radiation effects. All UV radiation effects are highly wavelength dependent, and better weighting functions that quantify the importance of spectral composition of UV radiation, as well as the exposure-response functions, have the potential to substantially improve the accuracy of our estimates of UV radiation effects in nature and the ability to scale results to broader geographic and temporal windows (**Fig. 4**). Similarly, while experiments with artificial UV lamps can be useful for elucidating some mechanisms of damage by UV radiation and response, more UV-exposure experiments with natural sunlight and monitoring data, including high resolution UV radiation, are essential to understanding the ultimate overall UV radiation effects on aquatic ecosystems.

Solar disinfection of surface waters of parasites and pathogens is likely one of the most valuable ecosystem services provided by UV radiation: many parasites and pathogens are inactivated by exposure to solar UV radiation.[231] We also know that eutrophication, glacial recession, recovery from acid deposition, and increases in extreme weather events related to climate change are increasing DOM and other UV-absorbing substances in many aquatic ecosystems, potentially reducing this valuable ecosystem service. For example, modeling exposure to UV radiation using the DNA action spectrum (sensitivity of DNA to damage by different UV wavelengths) suggests that higher DOM in many inland waters reduces the solar inactivation potential by up to ten-fold or more in surface waters.[227] What is missing are direct experimental tests of the hypothesised reductions in parasite and pathogen abundance, virulence, and infectivity as a function of DOM concentration and underwater exposure to UV radiation in nature, especially for human parasites. Filling this knowledge

gap is key to improving water security and human health as well as to understanding the role of solar UV radiation in controlling parasites and pathogens in aquatic ecosystems.

While we know that exposure to solar UV radiation is damaging to many aquatic organisms at all trophic levels, understanding the net effects of changes in exposure to UV radiation on ecosystems remains elusive. More studies on the simultaneous effects of UV radiation on multiple trophic levels are needed. There remains a substantial challenge to separate out the direct *vs* indirect effects of UV radiation as well as to separate the adverse effects of short wavelength UV-B radiation from the positive effects of longer wavelengths. For example, longer wavelength UV-A contributes to photosynthesis and primary production, which in turn provide food resources for primary consumers and orientation by zooplankton. UV-B radiation may also have positive effects, since the same short wavelengths of UV-B radiation that cause DNA damage, are also responsible for vitamin D production. Little is known about the role of UV-B radiation in regulating levels of vitamin D in aquatic organisms, although some fatty fish (e.g., salmon) are known to be a good source of vitamin D.[142] Vitamin D is essential to human health and well-being (see Chapter 2), and one might speculate it is important to a variety of aquatic organisms as well. While maintaining some low level of exposure of aquatic organisms to solar UV-B radiation may be healthy, almost nothing is known about their requirements for vitamin D or effects of vitamin deficiency. Laboratory experiments on the mechanisms that underlie responses to UV radiation, done under carefully characterised irradiance spectra, may create some advances in our understanding of the contrasting beneficial *vs* detrimental effects of UV radiation on different trophic levels. Larger scale approaches with wavelength-selective filters in mesocosms under natural solar radiation, as well as "natural" experiments along environmental gradients in regions of stratospheric ozone depletion, have the greatest potential to create new insights into the underlying mechanisms of response of multiple trophic levels to exposure to UV radiation. These insights into the net effects of UV radiation on aquatic food webs would assist in effective management of water quality, harmful algal blooms, and fisheries productivity, as well as understanding effects on aquatic biodiversity.

Simultaneous changes in climate and other environmental factors interact with the effects of UV radiation, making it difficult to separate out the net effects of UV radiation on observed long-term trends of change in aquatic ecosystems. Inland waters and oceans differ greatly in their size and ecosystem structure as well as the rates and types of environmental change. These differences will have an interactive influence on the effects of UV radiation on any given aquatic ecosystem. For example, increases in atmospheric CO_2 are acidifying the world's oceans as well as some reservoirs and lakes. Yet across major regions of northeastern North America and northern Europe, pH has increased by as much as a full pH unit related to decreases in anthropogenic acid deposition and increases in extreme precipitation events. These increases in pH are accompanied by up to two-fold or greater decreases in transparency of water to UV radiation in inland waters, and potentially similar changes in coastal estuarine environments. While these largely terrestrially-driven changes will have little effect on open oceans, deposition of dust may interact with nutrients to alter water transparency and effects of UV radiation, even in these vast, nutrient-limited ecosystems. While long-term records show changes in the structure and function of aquatic ecosystems, available data on transparency to UV radiation are too limited to separate the contrasting effects of changes in pH, transparency, and other factors such as nutrients in inland *vs* marine waters.

Plastic pollution is increasing in aquatic ecosystems, especially in coastal and open oceans (see section 5.2 and Chapter 7). UV radiation plays an important role in degrading these

plastics, but this degradation produces microplastics and nanoparticles that are taken up into aquatic food webs by zooplankton with unknown fate and effects. Concentrations of microplastics in aquatic food webs pose possible threats to food security, but very little is known about whether these plastics are essentially inert, or toxic to organisms that consume them. Does degradation of plastics by UV radiation lead to a sink that reduces plastic pollution in the environment? Or does it increase their toxicity by enhancing degradation and channelling them into food webs where they threaten food supplies? Phototoxicity, an increase in toxicity of certain compounds such as polycyclic aromatic hydrocarbons when exposed to UV radiation, is well known. But there is little information on the phototoxicity of the products of environmental transformation of other chemicals in aquatic ecosystems.

Finally, assessment of how stratospheric ozone-driven climate changes in the southern hemisphere are affecting biodiversity have only just begun and so far, do not yet include many important economic species such as those for fisheries. A better understanding of the proportion that can be attributed to stratospheric ozone depletion would assist with predicting likely future scenarios as the ozone layer recovers.

Filling these knowledge gaps may have important implications for food and water security. Valuable aquatic ecosystem services that are affected by UV radiation range from supplying critical food resources for a major portion of the world's population, to the sequestration of atmospheric carbon dioxide by the oceans and inland waters, to the ability of solar UV radiation to disinfect surface waters of parasites and pathogens, and to the preservation of biodiversity.

8 Conclusions

Stratospheric ozone dynamics and climate change interact strongly with solar UV radiation to control the exposure of aquatic ecosystems to underwater UV radiation, which has both beneficial and detrimental effects on aquatic organisms. The effectiveness of the Montreal Protocol has curtailed the potentially catastrophic high levels of exposure to UV radiation envisioned in the "world avoided" scenario of very high levels of stratospheric ozone depletion. Given the stabilising and recent evidence for recovery of stratospheric ozone, climate change and other environmental variables are now the most important driving factors changing exposure to UV radiation in aquatic ecosystems. In waters of high transparency, UV radiation is still recognised as potentially damaging to organisms at all trophic levels. While most organisms have some level of behavioural avoidance, photoprotection, or photoenzymatic repair that reduces the negative effects of UV, there is still extensive evidence that UV radiation is an important regulator of community structure as well as ecosystem-level processes. For example, incorporating UV photoinhibition into models of primary production in the world's oceans reduces estimates of primary production by about 20%.[150] Reductions in transparency of water related to increases in terrestrially-derived DOM can provide a refuge from damaging UV radiation that enables the survival of UV-sensitive planktonic predators that in turn decimate their prey.[129] In contrast, disinfection of surface waters by UV radiation is a valuable ecosystem service that is being compromised by reductions in transparency of water related to recovery of inland waters from acid deposition, and increases in heavy precipitation that increase inputs of UV-absorbing terrestrial DOM in inland and coastal waters.[227] The use of artificial sunscreens threatens the integrity of aquatic ecosystems near public beaches where concentrations of these toxic compounds are high enough to damage corals, sea urchins, insect larvae, phytoplankton, crustaceans, and fish. Legislation to limit

the use of some artificial sunscreens creates new challenges for the cosmetic industry to produce less toxic compounds that are still effective at reducing sunburn and related skin cancers. Ultraviolet radiation breaks down plastic pollutants into microplastics that are ingested by zooplankton and passed up the foodweb, with unknown effects on food security as these microplastics are found in fish being sold in public markets. Stratospheric ozone depletion is altering the climate in the southern hemisphere with beneficial effects observed in some seabirds, including albatross and penguins, as well as in sea mammals such as seals, but also declines in corals and kelp beds have been reported. This combination of the positive as well as negative effects of UV radiation on aquatic ecosystems and the interactive effects of stratospheric ozone depletion and climate change necessitate continued vigilance and the need to increase our understanding of these complex interactions and consequences for aquatic ecosystems and associated human food and water security.

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5 Solar UV radiation in a changing world: Roles of cryosphere-land-water-atmosphere interfaces in global biogeochemical cycles

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Summary

Global change influences biogeochemical cycles within and between environmental compartments (i.e., the cryosphere, terrestrial and aquatic ecosystems, and the atmosphere). A major effect of global change on carbon cycling is altered exposure of natural organic matter (NOM) to solar radiation, particularly solar UV radiation. In terrestrial and aquatic ecosystems, NOM is degraded by UV and visible radiation, resulting in the emission of carbon dioxide (CO_2), carbon monoxide, as well as a range of products that can be more easily degraded by microbes (photofacilitation). On land, droughts and land-use change can reduce plant cover causing an increase in exposure of plant litter to solar radiation. The altered transport of soil organic matter from terrestrial to aquatic ecosystems also can enhance exposure of NOM to solar radiation. An increase in emission of CO_2 from terrestrial and aquatic ecosystems due to effects of global warming, such as droughts and thawing of permafrost soils, fuels a positive feedback on global warming. This is also the case for greenhouse gases other than CO_2, including methane, and nitrous oxide, that are emitted from terrestrial and aquatic ecosystems. These trace gases also have indirect or direct impacts on stratospheric ozone concentrations. The interactive effects of UV radiation and climate change greatly alter the fate of synthetic and biological contaminants. Contaminants are degraded or inactivated by direct and indirect photochemical reactions. The balance between direct and indirect

photodegradation or photoinactivation of contaminants is likely to change with future changes in stratospheric ozone, and with changes in runoff of coloured dissolved organic matter due to climate and land-use changes.

1 Introduction

Biogeochemical cycles involve the transformation of materials in the environment and their transport across interfaces between different compartments in the Earth system, i.e., land, water, atmosphere, and cryosphere (ice, snow and frozen ground), **Fig. 1**. These cycles govern changes in the concentration and form of carbon, nutrients, and contaminants that affect organisms and ecosystems. Biogeochemical cycles influence the concentration of trace gases in the atmosphere, including carbon dioxide (CO_2) and other greenhouse gases, as well as air pollutants. Conversely, biogeochemical cycles in terrestrial and aquatic ecosystems are affected by changes in climate and stratospheric ozone (O_3).

In this report, we assess current knowledge on biogeochemical cycles in the context of global change, including changes in stratospheric ozone, climate, land-use, and the interactions between these changes (**Fig. 1**). We concentrate on the biogeochemical cycling of carbon, precursors of reactive trace gases, and synthetic and biological contaminants. Within that very broad remit, we focus on the effects of solar UV radiation on these cycles. However, rather than the narrow focus on UV-B (280–315 nm) radiation that is appropriate for assessing depletion of stratospheric ozone in isolation, we now also consider the effects of UV-A (315–400 nm), as well as of short-wavelength visible radiation since both UV and visible radiation are expected to change because of environmental changes (see Chapter 1). For example, increases in the frequency and intensity of wildfires and, consequently, enhanced emissions of aerosols affect solar radiation in all the spectral ranges. This chapter not only assesses the role of solar UV and visible radiation on the transformation of materials within compartments of the Earth-system but also how global change affects the transport between compartments, for example land-water, cryosphere-water, land-atmosphere, water-atmosphere.

The transport of materials between land, the cryosphere, and water is strongly influenced by effects of global warming such as thawing of permafrost soils, more frequent and longer lasting heavy precipitation events in some regions of the Earth, and droughts and wildfires in other regions. Stratospheric ozone depletion and warming in polar regions influence weather patterns also in other regions of the southern and northern hemisphere. The major role of ozone depletion in Antarctica on regional climate in the southern hemisphere has been identified (see Chapter 1) with concomitant effects on terrestrial and aquatic ecosystems[30, 152] (see Chapters 3 and 4), and biogeochemical cycles.[60, 152] Similarly, in the northern hemisphere, stratospheric concentrations of ozone in the Arctic have been suggested to affect local climates, with a study showing that years with low Arctic stratospheric ozone in March coincided with colder than normal temperatures over southeastern Europe and southern Asia, but warmer than normal temperatures over northern Asia in March/April.[90] Furthermore, changes in the Arctic due to Arctic amplification (i.e., where the Arctic warms faster than elsewhere in response to rising greenhouse-gas concentrations[60, 67, 134]) not only affects climate in the Arctic but also at mid-latitudes of the northern hemisphere.[66, 101, 134, 179] This phenomenon is linked to the jet stream which changes as a consequence of Arctic amplification and loss of sea ice.[66, 153] As a result, weather patterns have become more persistent and weather extremes more likely.[134]

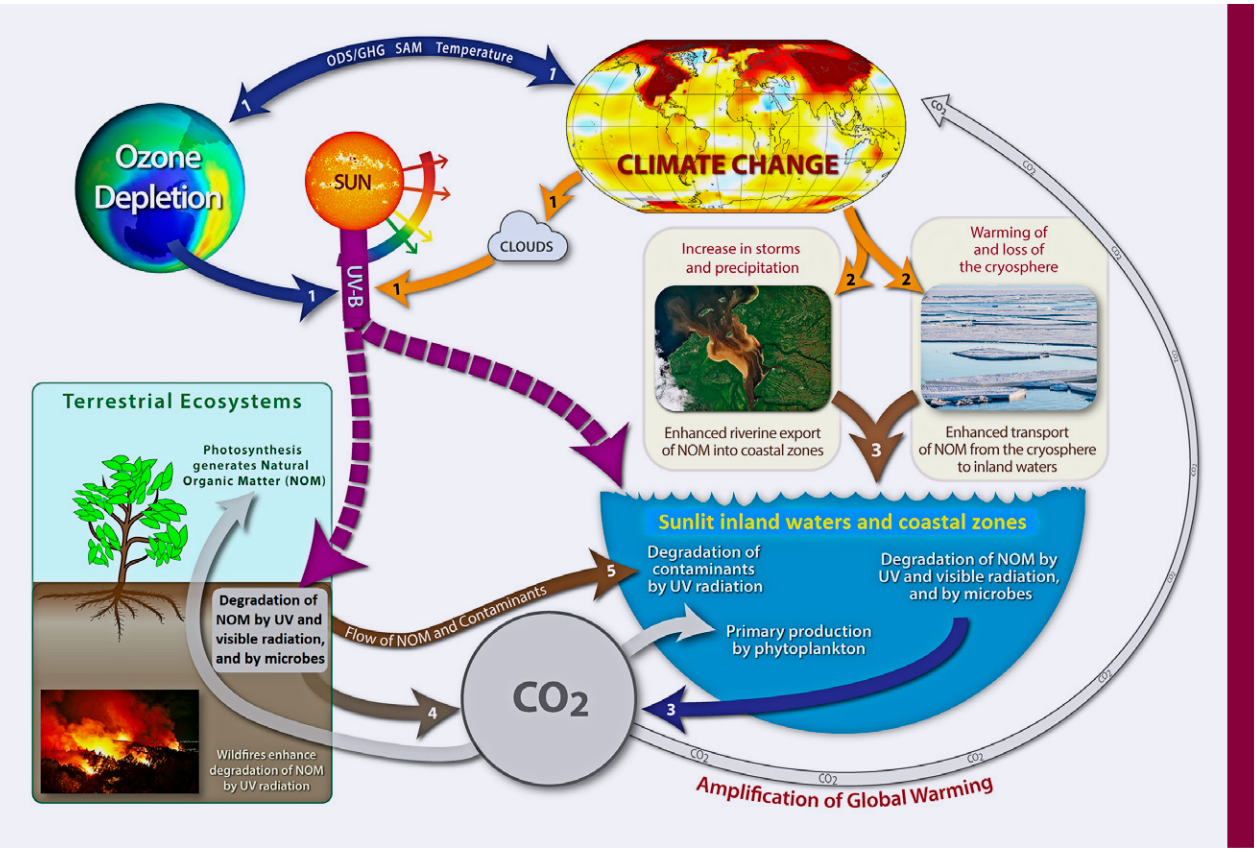

Fig. 1 **Interactive effects of solar radiation (UV and visible) and climate change on biogeochemical cycles. The numbers in the arrows refer to the following effects: (1) Stratospheric ozone concentrations are affected by ozone depleting substances (ODSs) and control the intensity of solar UV radiation (see Chapter 1). Clima-te change affects cloud formation and the intensity of UV radiation reaching the Earth's surface (see Chapter 1). Antarctic ozone depletion impacts local climates in the southern hemisphere via changes of the Southern Annular Mode (SAM) (see Chapters 1 and 3), while Arctic amplification influences local climates in the northern hemisphere. Interactive effects of solar UV radiation and climate change affect the biogeochemical production and fate of greenhouse gases, particularly CO_2, but also methane (CH_4), and nitrous oxide (N_2O) that impact climate and stratospheric ozone. (2) Important consequences of climate change are warming of and loss of the cryosphere, increasing frequency and intensity of droughts, wildfires, storms, and heavy pre-cipitation events in different regions of the Earth. (3) Loss of the cryosphere and increases in storms and heavy precipitation events result in the enhanced transport of natural organic matter (NOM) from land to wa-ter, where it is degraded to CO_2, CO, and other products by UV and visible radiation, and by microbes. (4) Similarly, degradation of NOM by UV and visible radiation, and by microbes occurs on soil surfaces. (5) Contaminants also undergo UV-induced degradation, either in direct or indirect photo-chemical reactions. Contaminants include organic contaminants, nanomaterials, microplastics, harmful algal blooms, and virus-es.**

Because of heavy precipitation events and loss of the cryosphere, e.g. thawing of permafrost soils, the flow of natural organic matter (NOM) from the land into water bodies is enhanced (**Fig. 1**, arrows 2 and 3). On land, NOM consists of plant and soil organic matter, whereas, in aquatic ecosystems, debris from algae and bacteria also contribute to NOM. However, in fresh and coastal waters, a large portion of NOM originates from terrestrial ecosystems and consists of terrestrial dissolved organic matter (tDOM), where a large part is coloured dissolved

organic matter (CDOM) and particulate organic matter (POM). Therefore, the focus of this assessment regarding carbon cycling is on the effects of solar radiation, particularly solar UV radiation, and climate change on the fate of terrestrial NOM, both on land and in water. The break-down of NOM on land and in water, a process which is influenced by exposure to solar radiation, releases carbon dioxide (CO_2, **Fig. 1**, arrows 3 and 4) and, to a smaller extent, carbon monoxide (CO) into the atmosphere.

Solar UV radiation also plays an important role in the degradation and inactivation of synthetic and biological contaminants in terrestrial and aquatic ecosystems, especially in the case of organic micropollutants that may pass through conventional sewage treatment plants without being degraded.[192] Among organic contaminants, antibiotics as well as pesticides are of increasing environmental concern. Pesticides usually enter aquatic ecosystems untreated from non-point sources.[184] Furthermore, some organic contaminants are persistent organic pollutants (POPs) with a long lifetime. Semi-volatile POPs can be transported over long distances in the atmosphere and may have environmental effects far from their point of origin, e.g., on penguins of the Southern Ocean.[59] In assessing the degradation of contaminants, the effects of climate change also have to be considered, particularly changes in the runoff of CDOM[205] (see Chapter 4). Models that consider changes in stratospheric ozone and thus UV-B radiation and effects of climate change help to predict rates of photodegradation or photoinactivation of contaminants in environmental systems. Section 5.3 discusses how models can help to quantify degradation of synthetic and biological contaminants in response to global change.

Changes in stratospheric ozone and climate also affect the biogeochemical cycling of trace gases other than CO_2, including carbon monoxide (CO), methane (CH_4), nitrous oxide (N_2O), and halogen compounds. CO is a key player in tropospheric chemistry since it competes with other trace gases for the hydroxyl radical (OH), for example, with CH_4, which is an important greenhouse gas. Emissions of CH_4 from natural sources including wetlands, permafrost soils, and wildfires contribute approximately 40% of total CH_4 emissions.[53, 158] These natural sources of CH_4 are affected by global warming and emissions of CH_4 further reinforce global warming. The third most important greenhouse gas is N_2O, following CO_2, and CH_4, which impacts the abundance of stratospheric ozone[64] (see Chapters 1 and 6). This trace gas is released from terrestrial and aquatic ecosystems and via thawing of permafrost soils. Biogeochemical processes in seawater and on the surface of the cryosphere also play an important role in the formation of halogen compounds other than chlorofluorocarbons (CFCs), which are precursors of reactive halogen species. Among the "natural" halogen compounds, brominated very short-lived substances (BrVSLS) are important trace gases for stratospheric ozone chemistry since they may reach the lowermost stratosphere and participate in depletion of stratospheric ozone. Reactive halogen species from natural sources also play an important role in tropospheric chemistry, e.g., as oxidants of gaseous elemental mercury.

Here we assess new findings in the realm of biogeochemical cycles under changing stratospheric ozone, solar UV radiation, and climate including the following sections: (2) Stratospheric ozone depletion and biogeochemical cycles: An overview of four decades of research; (3) Roles of interfaces and climate change in carbon cycling mediated by UV and visible radiation; (4) Natural emissions of trace gases that contribute to global warming and affect stratospheric ozone; (5) Effects of stratospheric ozone and climate change on UV-induced transformation of contaminants; (6) Feedbacks on global warming that are mediated by UV and visible radiation; and (7) Major advances and gaps in knowledge (with

respect to the interactive effects of solar radiation [UV and visible] and climate change on biogeochemical cycles).

2 Stratospheric ozone depletion and biogeochemical cycles: An overview of four decades of research

Assessing the effects of depletion of stratospheric ozone on biogeochemical cycles has been part of the remit of the Environmental Effects Assessment Panel since 1995. This, our seventh assessment, also follows the 30th anniversary of the Montreal Protocol and the ratification of its Kigali amendment in 2017. As well as assessing research progress over the last four years, it is timely in this assessment to place that recent research in the context of progress in research and policy over the last four decades.

Part of the success of the Montreal Protocol has been its influence on high quality science, not just the understanding of the mechanisms of stratospheric ozone depletion but also the understanding of the environmental effects of uncontrolled depletion of stratospheric ozone.[5] Conversely, the need for high quality science to underpin the Montreal Protocol has been a major stimulus for research across multiple scientific disciplines. As a result, understanding of the environmental effects of ozone depletion, above all, the effects of changes in solar UV-B radiation (280–315 nm), has been transformed over the last three to four decades. That transformation applies to understanding of the effects of UV-B radiation on biogeochemical cycling, which was very poorly developed prior to the 1980s. There was a small foundation of earlier research pertinent to this topic and, since that time much more has been added. For example, by the late 1970s it was well-established that UV radiation could be a significant factor in the degradation of organic pollutants (see e.g., ref.[143] and ref.[215]), humic substances (now generally included under the broad heading of dissolved organic matter (DOM)),[39, 100] and nitrate[214] in aquatic systems. By contrast, the role of solar UV radiation in the biogeochemistry of terrestrial ecosystems was effectively unexplored prior to the 1980s.

This research prior to the Montreal Protocol demonstrated that solar UV radiation could play a role in biogeochemical processes and identified fundamental photochemical mechanisms, thus laying the foundation for research stimulated by concerns over ozone depletion. Building on that foundation, research in the early 1980s revealed that the photochemistry of nitrate and coloured dissolved organic matter (CDOM) involved the generation of reactive oxygen species (ROS), such as OH. It became clear that ROS play a major role in the degradation of natural organic compounds as well as contaminants, and that metals (particularly iron) are involved in the production of OH in sunlit aquatic ecosystems.[218]

The Montreal Protocol also stimulated the first studies into the effects of UV-B radiation on biogeochemistry in terrestrial ecosystems. The first papers to investigate the effects of UV-B radiation on the decomposition of dead plant material ("litter") were not published until the mid-1990s. Following initial modelling studies,[125] it was confirmed that solar UV radiation could affect the rate of litter degradation[72] and enhance emissions of trace gases,[180] paving the way for substantial research over the last two decades, e.g., refs.[217, 60] Some of the trace gases that are emitted from these natural sources, e.g., nitrogen oxides (NO_x) and very-short-lived halocarbons, can affect concentrations of ozone in the troposphere and the stratosphere.[60]

This period of research stimulated primarily by the need to understand the effects of ozone depletion lasted, broadly, from the late 1980s until the beginning of this century. Since then, new advances in both science and policy have led to new perspectives on the role of UV radiation in biogeochemical cycling.

First, we now understand that the effects of solar UV radiation on biogeochemical cycles are not confined to the high irradiances or doses that would occur only with uncontrolled stratospheric ozone depletion. Field manipulations using wavelength-selective filters and laboratory-based studies with environmentally-relevant and well-defined treatments show that a wide range of biogeochemical processes respond significantly to variation in UV radiation within the ambient range. In addition, it is now clear that the results of depletion of stratospheric ozone other than increased UV-B radiation can have major effects on ecosystems that were not anticipated in earlier research. Antarctic ozone depletion has had a strong influence on climate in the southern hemisphere[207] (see Chapter 1) with concomitant effects on terrestrial and marine ecosystems (see Chapters 3 and 4) and biogeochemical cycles.[60, 152]

Second, we now have a much better understanding of the role of factors other than stratospheric ozone in determining surface irradiances of solar UV radiation, both UV-B and longer wavelength UV-A (315–400 nm). The effects of time of day, season and latitude on UV irradiances, all driven by the changes in solar elevation, have been well-defined for many years. However, quantification of the response of UV irradiances to stochastic changes in other factors, including cloud, air pollution and aerosols, continues to improve (see Chapter 1). There is also increased awareness that variation in surface irradiances, as typically measured by atmospheric scientists, is not the only factor affecting the exposure of organisms or ecosystems to UV-B radiation. The absorption or reflection of UV radiation by ice or snow may significantly affect the exposure to UV radiation at high latitudes or high altitudes (see Chapter 1). In terrestrial ecosystems, plant canopies greatly influence the exposure to UV radiation at the soil surface (see Chapter 3), while the exposure to UV radiation in aquatic systems is also substantially influenced by the effects of coloured dissolved organic matter (CDOM) on the penetration of UV radiation through the water column (also see Chapter 4).

Third, the successful implementation of the Montreal Protocol and its amendments has prevented uncontrolled, global ozone depletion[207] (see Chapter 1). While significant seasonal ozone depletion over the Antarctic has occurred annually since the 1980s, changes in total stratospheric ozone in other regions have been small and/or transient (see Chapter 1). Except for the effects of ozone "holes" over the Antarctic, and occasionally over the Arctic, measurable effects of changes in stratospheric ozone on level of surface UV-B radiation have generally been hard to identify against variation due to other factors (see Chapter 1). Looking ahead, ozone recovery over the Antarctic is expected to progressively reverse the seasonal increases in surface UV-B radiation measured there (see Chapter 1). Beyond the Antarctic, future trends in exposure to surface UV-B radiation will be driven partly by changes in stratospheric ozone and partly by changes in factors other than stratospheric ozone (see Chapter 1). These factors include cloud, air pollution, aerosols, ice and snow cover and DOM, which are all expected to be affected by climate change, with marked temporal and geographical variation in the magnitude and in some cases the direction of change (see Chapter 1 and 4).

Fourth, it is increasingly evident that knowledge of the effects of solar UV radiation on biogeochemistry is necessary to understand not only responses to environmental change but also the drivers of change. A primary example is the role of solar radiation in determining exchanges of CO_2 and other GHGs, for example, the release of CO_2 from plant litter or DOM,[15, 51, 217] but also changes in the uptake of CO_2 by aquatic organisms (see Chapter 4) and,

perhaps, terrestrial plants (see Chapter 3). Biogeochemical processes driven by sunlight are also pertinent to understanding other current environmental challenges, including the fate of dissolved pollutants such as pesticides or heavy metal compounds, or the increasing problem of plastics contaminating the environment (also see Chapters 4 and 7).

These new scientific perspectives, which have emerged progressively over several years[60, 217] are now framed by recent changes in the Montreal Protocol itself. The Protocol has evolved to control not just the original ozone-depleting substances, such as chlorofluorocarbons (CFCs) but their replacements, most recently hydrofluororcarbons (HFCs). The control of HFCs under the 2016 Kigali Amendment is notable because HFCs are not ozone-depleting substances but many are greenhouse gases.[207] As a result, as well as continuing to be the global mechanism for protecting the stratospheric ozone layer, the Montreal Protocol now includes a specific responsibility for protecting Earth's climate.

3 Roles of interfaces and climate change in carbon cycling mediated by UV and visible radiation

There are many aspects of climate change that affect biogeochemical carbon cycling by changing the exposure of natural organic matter (NOM) to UV and visible radiation on the surface of the Earth. Important effects are warming of and loss of the cryosphere and more frequent and longer lasting heavy precipitation events. In this section, we assess the interactive effects of solar radiation, particularly solar UV radiation, and climate change on carbon cycling across cryosphere-land-water-air. Solar UV and visible radiation play a role in the degradation of NOM to CO_2 and CO, a process that is often enhanced by climate change and can thus feedback to modify climate.

When plants die on land, the organic matter produced by photosynthesis is then decomposed and eventually transformed to inorganic carbon (CO_2 and CO). Although most of the carbon turnover is mediated by decomposer organisms, some decomposition of NOM is driven directly by solar UV and visible radiation through photochemical reactions that generate CO_2 (**Fig. 2**).[15, 31] The degradation of NOM by solar UV and visible radiation occurs on land and in fresh and marine waters after the transfer of NOM from land to water. One of the key controls of photodegradation of NOM on land and in water are compounds that absorb solar radiation. One example is lignin, a compound that provides structural support for plants and is almost exclusively found in plants of terrestrial origin.[204] Lignin has been shown to be one of the principal light absorbing compounds in decaying plant material.[13, 14, 104, 126] In addition to the production of CO_2 and CO, photodegradation of NOM on land and in water yields smaller organic compounds that are more bioavailable to microorganisms, a process called photofacilitation[14, 126, 179] (also see Chapter 3). In this section, the term "photodegradation" is used to include the integrated effects of solar radiation through photochemical degradation of NOM and photofacilitation of microbial decay.

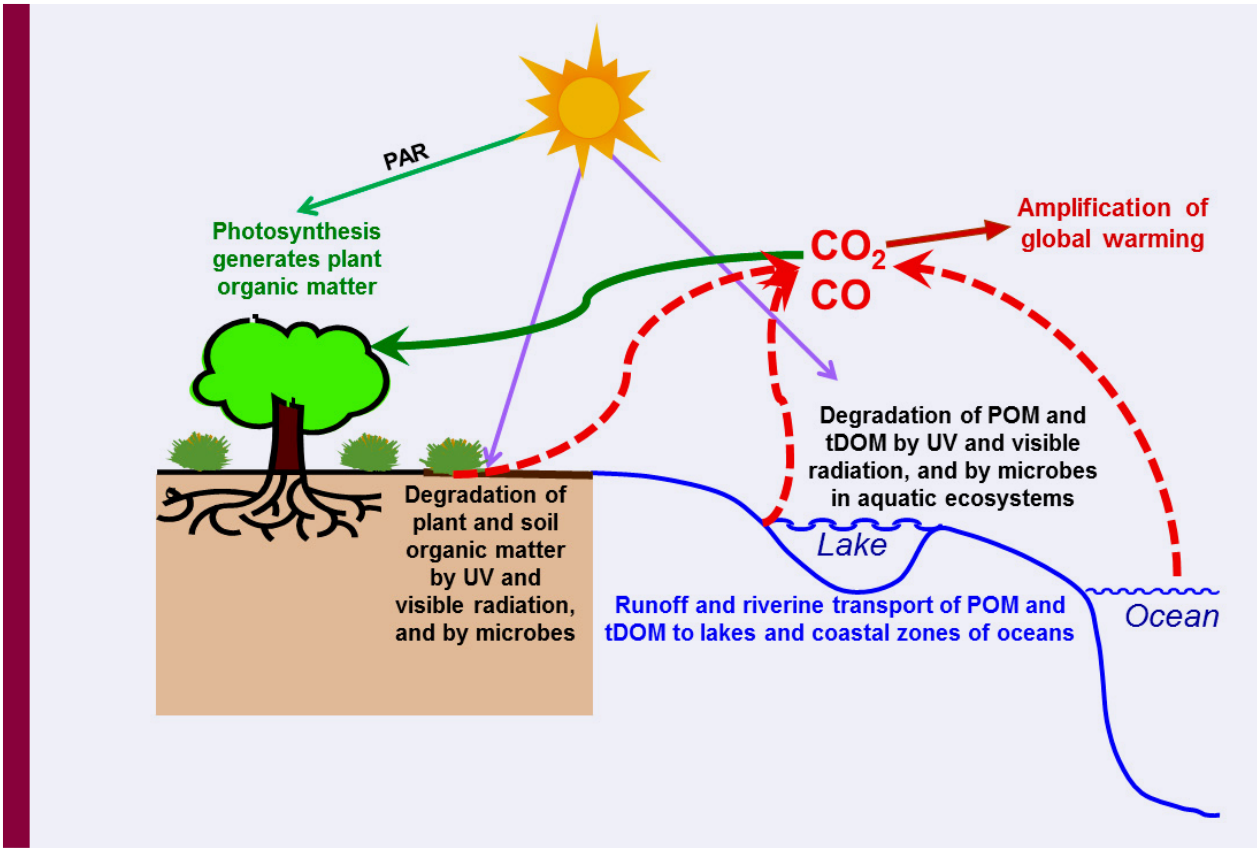

Fig. 2 **Plants take up CO_2 from the atmosphere and convert it to plant organic matter, of which light-absorbing lignin is a major component. When plants die, plant and soil organic matter is decomposed by soil microbes to CO_2 and CO that is returned to the atmosphere, and to smaller pools of organic matter (i.e., particulate and terrestrial dissolved organic matter; POM and tDOM respectively). POM and tDOM are flushed to streams, rivers, and lakes in rain and snow, and to coastal waters via riverine export. On land and in sunlit surface waters, UV and visible radiation help decompose plant organic matter, POM, and tDOM to CO_2 and CO. PAR, Photosynthetic Active Radiation (400–700 nm).**

The fundamental mechanisms of photodegradation of NOM are the same on land and inwater. The rate of degradation of NOM via direct photoreactions depends on the quantum yield (efficiency of a photoreaction), and on the rate of light absorption by NOM. The latter is influenced by many factors that are susceptible to changes in stratospheric ozone, climate, and land-use, including the intensity of solar radiation, particularly solar UV radiation at the surface of land or water, and the concentration and absorption properties of NOM. Thus, there are several common ways in which the relative importance of photochemical degradation on land and in water may be affected by climate and change in land-use. Fundamentally, any change in solar radiation (i.e., changes in cloudiness or air pollution events) may contribute to changes in photodegradation of NOM on land and in water. In addition, changes in cover by vegetation can alter the exposure of NOM to solar radiation (i.e., canopy on land or vegetative shading of streams).[11, 20]

In aquatic ecosystems, terrestrially-derived dissolved organic matter (tDOM) can also be degraded via indirect photochemical reactions with the help of photosensitisers that absorb solar (mainly UV) radiation. Important photosensitisers are CDOM, nitrate (NO_3^-), and iron

compounds (section 5.1). Upon absorption of sunlight, photo-excited sensitisers undergo reactions involving dissolved oxygen (O_2) to produce reactive oxygen species (ROS), such as OH, superoxide ($O_2^{\cdot-}$), hydrogen peroxide (H_2O_2), and singlet oxygen ($^1O_2$) (**Fig. 3**).[46, 179, 210] These ROS can completely degrade tDOM to CO_2[136, 186] or partially degrade tDOM, resulting in organic matter altered in chemical composition[193] to be more or less labile to microbial degradation to CO_2 (**Fig. 3**).[50, 200] In addition, ROS are harmful to aquatic microbes[210] (see Chapter 4) and may suppress the degradation of tDOM by microbes.[8, 93] The relative importance of ROS for increasing the bioavailability of tDOM and for negative effects on microbial communities and their activities remains an open question.

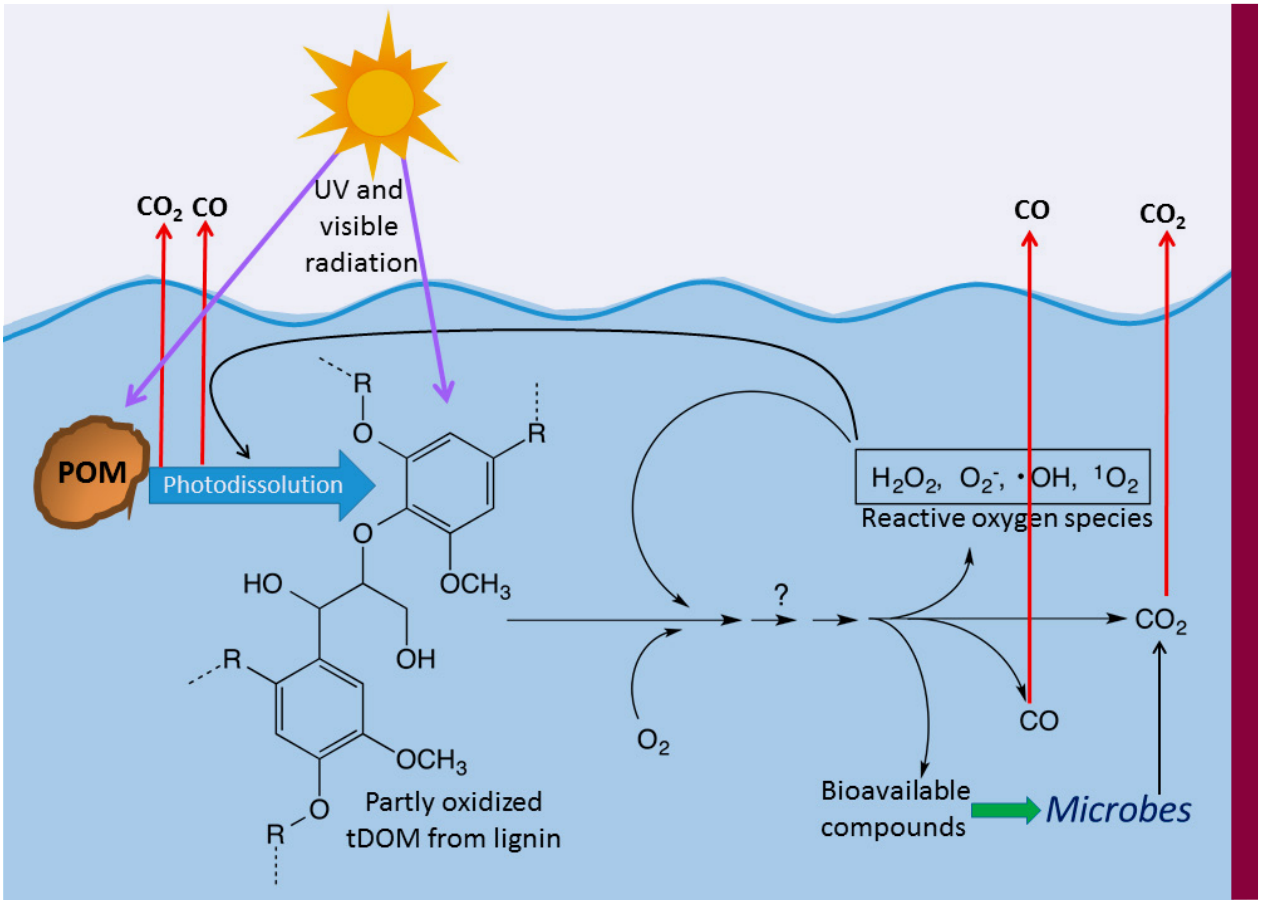

Fig. 3 **Terrestrial dissolved and particulate organic matter (tDOM and POM, respectively) absorb solar UV and visible radiation in fresh and marine waters. This light absorption results in the photodissolution of POM and the photodegradation of tDOM to greenhouse gases (mainly CO_2), and to smaller molecules that are readily degraded by microbes to CO_2 (i.e., respiration). Reactive oxygen species produced by photo-excited tDOM and POM help to breakdown tDOM and POM to greenhouse gases and smaller organic molecules (modified from Sulzberger and Arey, 2016[179]).**

Including photodegradation as a pathway for the production of greenhouse gases from terrestrial and aquatic ecosystems improves models of carbon cycling on land[1] and improves understanding of controls on emissions of greenhouse gases from inland and marine waters.[51, 98, 145, 188] For example, in environments where biological decomposition of NOM is relatively slow,[51] it is now recognised that photodegradation of NOM on land and in water are

important components of the carbon cycle. On land, photodegradation of NOM is important in arid and semi-arid environments where solar UV and visible radiation are high and microbial decomposition is limited by water and availability of carbon.[12] In contrast, photodegradation of NOM is important in aquatic ecosystems in Arctic and boreal regions, despite the relatively lower solar UV and visible radiation in these high latitudes compared to temperate and tropical regions. Due in part to slow rates of microbial decomposition in the cold waters at these high latitudes, photodegradation of NOM in aquatic systems is important.[51] Given these environmental controls on the relative importance of photodegradation of NOM on land and in water for carbon cycling, e.g., dryness *vs* humidity on land, temperature in water, it follows that there are key differences in how these processes may shift in magnitude or location in response to human-caused global changes. These changes may occur through land-use, climate change, and stratospheric ozone depletion in Antarctica (also see Chapters 1 and 3), where the latter two result in global warming and altered precipitation patterns. Effects of global changes on the photodegradation of NOM on land and in water are discussed in the next sections.

3.1 Effects of global change on photodegradation of natural organic matter on land

Photodegradation of NOM has been observed in the field,[15, 31, 74, 155] and the laboratory.[103, 104] Several of these studies have demonstrated that, at the ecosystem scale, the loss of carbon via photochemical degradation of NOM in ecosystems with marked seasonality of rainfall could be on a par with microbial respiration. The contribution of photochemical degradation of NOM *vs* biotic degradation is often difficult to quantify since these two processes occur simultaneously in most ecosystems, and many of the products of these reactions (e.g., CO_2) are identical. Nevertheless, there is increasing confidence that, particularly in semiarid ecosystems, the unexplained high rates of decomposition that occur may be directly related to carbon loss through exposure to solar UV and visible radiation.[12, 19]

In addition to the photochemical degradation of lignin and other light-absorbing organic compounds of plant litter, exposure of plant litter to UV and short-wavelength visible radiation can facilitate biological degradation of NOM in terrestrial ecosystems[14, 17, 70, 73, 195] (also see Chapter 3). In dryland ecosystems, modeling of photochemical and photofacilitated degradation of NOM demonstrates substantial contributions to carbon turnover in terrestrial ecosystems.[1] The suggested role of photofacilitation is increased microbial access to labile carbohydrates in litter following photochemical degradation of lignin[14] (see Chapter 3 for a more detailed review). Thus, through the effects of photofacilitation, solar UV and visible radiation play a major role in carbon turnover in a wide range of mesic (moist) terrestrial ecosystems.[14]

3.2 Land-use change and photodegradation

Changes in land-use continue to be one of the major factors affecting terrestrial ecosystems around the globe. Future conversion of ecosystems for agricultural use, particularly in South America and sub-Saharan Africa,[159] extraction of wood and other products, or planting of exotic species for potential carbon mitigation, will all place pressure on soils and carbon reservoirs in terrestrial ecosystems.[171] The effects of these changes on photodegradation of NOM have not been considered as of yet, but could have important consequences for carbon cycling at regional and global scales. Afforestation, the planting of woody vegetation in

areas that were previously dominated by herbaceous vegetation, can have surprising effects on carbon turnover. In a comparison of paired sites with pine plantations and natural counterparts of grassland and steppes, afforestation caused more than a 60% reduction of the decomposition of litter in arid zones.[11] Moreover, the relationship between the decomposition of litter in the paired afforested and natural vegetation was largely explained by differences in the interception of solar radiation before it reached the surface of the soil.[11] These results suggest that conversions due to agriculture, deforestation, and afforestation could have large impacts, positive or negative, on carbon cycling via changes in the interception of solar UV and visible radiation.

Climate change due to human activity has been documented worldwide and is of growing concern due to its impacts on the functioning of natural ecosystems. In this context, two important global changes in terrestrial ecosystems, droughts and wildfires, are of relevance to the photodegradation of plant litter. Due to the reduction of plant cover, which enhances exposure of plant litter to solar radiation,[11] photochemical degradation of NOM tends to increase under conditions of drought or extreme aridity.[4, 88] In addition, photofacilitation can play an important role in arid ecosystems since this process stimulates microbial breakdown of plant litter.[14, 56, 70] In summary, an important impact of global warming on terrestrial ecosystems is increased exposure to solar UV radiation of previously unexposed NOM. This is due to decreased plant cover and reduced interception of solar radiation. Thawing of permafrost soils and combustion of aboveground vegetation can also result in increased exposure of NOM to solar UV and visible radiation (see the following section).

3.3 Role of global change on photodegradation of tDOM and POM in fresh and coastal waters

In this section, we assess the effects of UV and visible radiation, as well as global change, on the emission of CO_2 and CO from fresh and coastal waters via degradation of tDOM. NOM produced by plants moves from land to water in particulate and dissolved form (POM and tDOM, respectively) (see **Fig. 2**). Most of the terrestrial carbon flushed from land to water is in the form of tDOM[2] and, thus, most studies have focused on the photodegradation of tDOM. However, photodegradation of POM is now recognised as important, especially in coastal waters, and we highlight some recent work in this area (section 3.3.2). Loss of the cryosphere is a major global change that enhances the exposure of tDOM to UV and visible radiation (discussed in section 3.3.3).

3.3.1 Photodegradation of tDOM in fresh and coastal waters

To balance terrestrial carbon budgets, the degradation of tDOM in aquatic systems must be accounted for.[26, 43, 149] Studies published within the last five years have challenged the understanding that microbial decomposition of tDOM was much more important than photodegradation of tDOM. For example, current estimates are that 10–30% of the CO_2 released from Arctic and boreal waters comes via photodegradation of tDOM.[51, 98, 188] Given that freshwaters account for 40% of the net exchange of carbon between land and the atmosphere in the Arctic,[117] CO_2 released from freshwaters via photodegradation of tDOM is important in regional and global carbon budgets. More research related to photodegradation of tDOM in freshwaters is needed since in North American and European freshwaters, concentrations of tDOM have been increasing, a trend called “browning”, which indicates increased inputs of

light-absorbing tDOM.[206] The causes of browning are currently under debate and may vary by region (also see Chapter 4).

tDOM is exported into coastal waters largely by rivers. Flooding of riparian zones due to heavy precipitation events results in increased export of tDOM into marine environments.[106] Decades of research have documented the importance of photodegradation of tDOM to CO_2 and CO once this organic matter is exported from rivers to the coastal ocean (reviewed in refs[60] and[126]). For example, estimates are that from 3–40% of tDOM exported to coastal waters from rivers can be converted to CO_2 and CO within months to a few years.[126] Photodegradation of tDOM to CO_2 in the ocean has been estimated to offset the net air–sea flux of CO_2 by about 8–28%.[145]

Enhanced runoff also increases the supply of nutrients, for example, iron to phytoplankton. Its availability to phytoplankton is affected by solar UV radiation,[178] and by the interactions with other global changes such as acidification of aquatic ecosystems.[89, 162, 178] While iron is an important micronutrient for phytoplankton (see Chapter 4), it can also catalyse the photochemical degradation of tDOM (section 3.3.3). Hence, enhanced export of iron from land to water could enhance uptake of CO_2 via primary production but also release of CO_2 via photodegradation of tDOM. The balance between uptake and release of CO_2 at coastal interfaces depends on complex interactions.[76] Based on air-sea CO_2 flux measurements, Laruelle and coauthors[102] found that the global coastal ocean is a much smaller sink of CO_2 (~0.2 Pg C yr^{-1}) than was previously thought, and that many coastal regions are net sources of CO_2.

In addition to photodegradation of tDOM to CO_2 and CO, ~70% of tDOM is partially photodegraded (i.e., altered in chemical composition) by sunlight during riverine transit to the Arctic Ocean.[51] This partial degradation of tDOM by UV radiation can facilitate or slow microbial respiration of tDOM to CO_2.[200] It has been known for a long time that photodegradation of tDOM breaks down large biomolecules like lignin into smaller, simpler compounds that microbes use for energy with the production of CO_2 (see above and **Fig. 3**). Hence photofacilitation also plays an important role in aquatic ecosystems and supports aquatic food-webs (also see Chapter 4). What is less well-known, and a focus of current research is how important this photofacilitation process is for the cycling of carbon in freshwaters in a quantitative way. Although currently poorly quantified, the effect of photochemical degradation of tDOM on its conversion to CO_2 by microbes is probably substantial given that studies show that microbial respiration of tDOM to CO_2 can be increased or decreased by more than two-fold after tDOM has been degraded by UV and visible radiation.[47]

3.3.2 Photodissolution of POM in fresh and coastal waters

Both tDOM and POM enter aquatic ecosystems when soil organic matter runs off from land to water (**Fig. 2**). In sunlit surface waters, POM can be altered by photochemical reactions (photodissolution) to yield dissolved organic matter[95, 105] (i.e., tDOM that can undergo further photodegradation), CO_2 and CO[172] (**Fig. 3**). The photodissolution of POM to tDOM can also occur via indirect photoreactions, involving OH.[10] In contrast to photodissolution of POM of distinct terrestrial origin, more work has focused on photodissolution of resuspended estuarine sediment and POM in coastal waters.[62, 81, 95, 114] POM from resuspended sediment in coastal waters likely reflects a mixture of sinking particles from different sources of NOM. These sources include terrestrially-derived POM exported from rivers to coastal waters as well as autochthonously-derived POM produced from algal and bacterial detritus.[61, 81, 113, 144]

Studies have shown that production of DOM via photodissolution of POM from resuspended sediments resulted in fluxes of DOM that were larger than benthic and riverine fluxes of DOM to coastal waters.[95] Others have suggested that 5–15% of POM could undergo photodissolution before settling in coastal waters.[112] However, a review highlighted the lack of quantitative information on the contribution of photodissolution of POM to carbon cycling and fluxes of carbon to and from coastal waters.[126] Quantifying photodissolution of POM requires an integration of environmental factors including the turbidity of the water column (which controls the UV and visible light exposure of POM) and the apparent quantum yields of photodissolution of POM to products,[62] as well as separating out contributions from biological decomposition. These sunlight-induced changes in rates of photodissolution of POM have consequences for the biogeochemical cycling of POM in aquatic ecosystems including the transfer of POM into bottom sediments.

3.3.3 Warming of and loss of the cryosphere generally increases the likelihood that terrestrial dissolved organic matter will be degraded by UV and visible radiation

It is now recognised that photodegradation of tDOM can account for a substantial fraction of the total CO_2 released from Arctic surface waters. Currently, photodegradation may contribute 30% of the CO_2 emitted from the water column of Arctic waters,[51] which is important because these waters account for 40% of the net atmosphere-land exchange of carbon.[117] For example, thawing of permafrost soils in Arctic and boreal regions is predicted to increase export of tDOM to inland and coastal waters.[57, 183] tDOM of permafrost origin (i.e., previously frozen organic matter) contains less light-absorbing CDOM on a per carbon basis, compared to tDOM draining from the actively thawed soil layers at high latitudes.[177, 197, 200] This implies lower rates of absorption of UV radiation and thus lower rates of photodegradation in the water column.[48, 49] However, lower CDOM content of permafrost tDOM is offset by higher apparent quantum yields of the photochemical reactions that result in the formation of CO_2, CO, and organic compounds that strongly facilitate microbial respiration.[47, 83, 188, 199] Thus, increasing export of permafrost tDOM from land to water likely means that photodegradation of tDOM may become an even more important source of CO_2 from inland waters of the Arctic.[199]

Another reason why photodegradation of tDOM will continue to be important in a warming Arctic is because the export of light-absorbing tDOM from land to water and the time of exposure of tDOM to UV radiation in sunlit waters, are dependent on the hydrology of the watershed. Every year during spring in the Arctic (i.e., May – June), snow melt on land flushes tDOM from soils to rivers, ponds, and lakes, resulting in an annual peak in the concentration of light-absorbing tDOM in sunlit surface waters.[65, 68, 108] During this period of ice and snow melt, and flooding on land, the storage of river water in lakes and on floodplains can be substantial, e.g., up to approximately 50% of the flow of Mackenzie River in the Canadian Arctic can be stored on the floodplain during this time.[69] Retention of Mackenzie River water stored on the floodplain during spring snowmelt and floods increases the time that tDOM is exposed to UV radiation. This is because the timing of snowmelt and spring floods coincides with times of peak solar irradiation in the Arctic. The longer the time tDOM is exposed to UV radiation, the more this carbon can be photodegraded to CO_2 and CO. In addition, during spring floods, river water is spread in a thin layer (~2 m thick) across an area more than 11,000 km^2 in size,[69] which also increases opportunities for tDOM in the water to be photodegraded. This effect of river flooding on annual greenhouse gas production through photodegradation of tDOM in Arctic waters is not currently accounted for in regional carbon budgets.[69] This would

be important, given that snowmelt and spring flooding may be happening earlier due to warming.

Warming at high latitudes is accelerating melting of ice on rivers, ponds, and lakes and of snow on land; furthermore, it also changes the timing of the melt. For example, melting of ice and snow on water[52] and land[169] are occurring earlier in the Arctic spring. Earlier retreat of ice and snow has increased the number of days tDOM on inundated land or in water is exposed to UV radiation on average by one day per year from 2000–2013 across the Arctic. Some areas of the Arctic show a faster trend in loss of ice and snow[32] Earlier melt of ice and snow on freshwaters and land in May and June means more overlap with the time of the year when the sun angle is at its highest (and thus, UV radiation reaching the surface is most intense in the Arctic), and when concentrations of light-absorbing tDOM are also at their highest of the year.[65, 108] Thus, this earlier melt of ice and snow on water and land in the Arctic can substantially increase photodegradation of tDOM to CO_2 and CO[51] by increasing the time this carbon is exposed to UV radiation.

Other changes in Arctic and boreal hydrology influence the duration of exposure of tDOM to UV radiation. These changes include an increase or decrease in the number and surface areas of small ponds, depending on the regions of the Arctic and boreal zones,[7, 36, 132] as well as changes in the connectivity of lakes in Greenland.[133] In addition, increased turbidity of freshwaters from thawing of permafrost[91] could decrease exposure of tDOM to UV radiation. Any change in the exposure of tDOM to UV radiation in lakes and ponds may affect photodegradation of tDOM to greenhouse gases.[49, 133]

The intensity and frequency of droughts and wildfires are increasing worldwide as a result of changes in climate and land-use,[23, 80, 92, 134, 156, 206] and in the southern hemisphere, this is being further enhanced by the effect of ozone depletion on climate (see Chapter 3). In the Arctic, the current and projected increases in wildfires in boreal forests and Arctic tundra,[87, 189] could have multiple consequences for boreal and Arctic ecosystems as wildfires are sources of greenhouse gases (including CO_2, CO, and CH_4), and of volatile hydrocarbons to the atmosphere.[96, 139] Increasing frequency and extent of fires in the Arctic tundra[87] could influence photodegradation of tDOM in several ways. Fires in the Arctic tundra and boreal forest have been shown to transform tDOM into compounds called black carbon[202] (also see Chapter 4), particularly at high fire temperatures (> 600–700°C).[157] Black carbon is a component of tDOM with higher extinction coefficients (where extinction coefficients reflect the absorption properties of components) and thus higher susceptibility to photodegradation.[194, 202] Wildfires also affect the thawing of permafrost soils; the loss of permafrost with warming after fire has been linked to reduction of the insulating surface organic layer.[33] For example, up to 0.5 m of settlement was observed during thaws after recent fires in Alaska, causing impoundment of water and further thawing of permafrost.[33] Another effect of wildfires is the decrease in UV and visible radiation reaching the surface of aquatic systems because of the generation of short-lived aerosols that act as cloud-condensation nuclei.[206] As a consequence, rates of tDOM photodegradation may decrease. Widespread wildfires in Alaska have resulted in substantially lower UV and visible light in the Alaskan Arctic for the few days in the summer when rivers and lakes are ice-free and otherwise exposed to sunlight. Thus, the fire-related decrease in solar UV and visible radiation reaching the water surface could offset the warming related loss of snow and ice that increase exposure of tDOM to UV radiation. However, at present, no study has investigated the effect of fire on UV radiation reaching Arctic or boreal surface waters.

Finally, there is some indication that thawing permafrost may increase export of iron to Arctic and boreal inland waters (**Fig. 4**),[44] a trend recently reported for North American and European surface waters.[28] Increased concentrations of iron in sunlit surface waters may enhance photodegradation of tDOM via various mechanisms,[178] for example, by increasing the rates of light-absorption by tDOM,[211] by producing reactive oxygen species (ROS) that degrade tDOM,[136] and by catalysing other reactions that photodegrade tDOM.[77, 199] For example, Page and co-workers[136] concluded that degradation of tDOM by ROS, produced in UV-induced iron cycling, could account for 5–10% of the CO_2 formed from photodegradation of tDOM in Arctic waters.

Fig. 4 **The red colour in the Saviukviayak River (Alaskan Arctic) is due to high concentrations of iron flushed from land to water. Once in the sunlit river, iron plays a role in photochemical reactions. Photo credit: R.M. Cory.**

4 Natural emissions of trace gases that contribute to global warming and affect atmospheric ozone

Several gases released from terrestrial and aquatic ecosystems, or from the surface of the cryosphere contribute to global warming and changes in stratospheric ozone concentrations. Some of these gases are highly reactive in the troposphere and in the stratosphere. The following sections discuss the formation and environmental significance of CO, CH_4, and nitrogen- and halogen-containing trace gases.

4.1 Carbon monoxide

Carbon monoxide is a gas that plays an important role in tropospheric chemistry by contributing to the formation of ozone and by greatly impacting the concentration of OH (also see Chapter 6). On a regional scale, CO participates in gas-phase reactions that control local concentrations of ozone and peroxides. On a global scale, CO competes with atmospheric CH_4 for OH,[176] thus decreasing the atmospheric capacity to oxidise CH_4, and indirectly affecting the lifetime of this important greenhouse gas. Although CO itself only weakly absorbs infrared radiation from the Earth, the cumulative indirect radiative forcing of CO, taking into account its effects on the components CO_2, CH_4, and O_3, may be even larger than that of the third most important greenhouse gas, N_2O.[128]

Major sources of CO include direct production from burning of fossil fuels and biomass, e.g. wildfires, and tropospheric oxidation of hydrocarbons.[213] Emissions of CO from both terrestrial and aquatic ecosystems are a balance between production, which has light-dependent and light-independent mechanisms, and microbial processes that consume CO. Consumption of CO typically exceeds production at night, while photochemical production

becomes dominant during daylight. The resulting significant diurnal variations in CO fluxes have been confirmed in both terrestrial[60, 141] and aquatic systems.[126]

Additional studies since our last assessment have confirmed that the production of CO in the ocean and freshwaters occurs primarily via photodegradation of CDOM (section 3). Photodissolution of POM to CDOM also contributes to the formation of CO[60, 126, 145, 172, 173] (section 3.3.2 and **Fig. 3**). The measured average ratio of CO_2/CO is close to 20 in marine systems and somewhat lower in freshwaters.[60] In terrestrial ecosystems, it is well-established that photodegradation of plant litter from a variety of species yields CO, in addition to CO_2 (e.g., refs[60, 141]; and section 3.1). Emissions of CO can be enhanced by fires, not just during the fire itself[37] but also in the longer term, since charring transforms organic matter into a broad spectrum of organic constituents (including black carbon), which can emit CO and other gaseous products via photodegradation[157, 194] (section 3.3.3).

Given these mechanisms, the production of CO is likely to be affected by various elements of environmental change, for example, by increased inputs of CDOM into aquatic systems (also see Chapter 4), and increased aridity in terrestrial systems (section 3.1 and Chapter 3). In aquatic ecosystems, the concentrations of CDOM and POM may be increased by floods. Photoproduction of CO from POM may be as important as that from CDOM, depending on the season.[172] The ratio of the apparent quantum yield of CO photoproduction from POM and CDOM, ΦCO-POM/ΦCO-CDOM, has been shown to increase from UV to visible radiation.[172] On the balance of evidence, these environmental changes are likely to increase the production of CO by solar radiation but the magnitude of this increase remains unclear, especially relative to changes in other processes that affect the production and consumption of CO.

4.2 Methane

UV-induced production of methane (CH_4) from plant material discussed in previous assessments is no longer considered to be a significant source of CH_4.[30] Nonetheless, we consider CH_4 briefly here because it is not only a potent greenhouse gas but it also indirectly impacts stratospheric ozone. In the Executive Summary of the Scientific Assessment of Ozone Depletion: 2018[207] it is stated: "Outside the Antarctic, CO_2, CH_4, and N_2O will be the main drivers of stratospheric ozone changes in the second half of the 21st century, assuming full compliance with the Montreal Protocol". In order to predict trends in stratospheric ozone, it is, therefore, important to assess biogeochemical sources of methane, as well as its atmospheric loss-processes.[41, 64]

The contribution of CH_4 to radiative forcing is about half of that of CO_2 if indirect effects of CH_4 emission, such as the production of stratospheric water vapour, also are taken into account.[128] The global atmospheric concentrations of CH_4 have been increasing in the past three to four decades at various rates. The present net growth rate of CH_4 is about 5–10 ppb yr^{-1} and is higher than it has been for the past 20 years.[34, 53] Approximately 60% of global emissions of CH_4 were anthropogenic in the decade 2003–2012[53, 158] through agriculture, waste, and fossil fuel extraction and use. Over the industrial era, concentrations of atmospheric CH_4 rose from about 720 ppb before industrialisation to over 1,850 ppb in 2017.[146] Methane is also formed via biogeochemical processes and sources of CH_4 may vary seasonally. For example, in the winter, concentrations of CH_4 in the Arctic troposphere are mainly controlled by anthropogenic emissions including sources from Russian fossil fuel industries, whereas, in the summer, emissions from wetland and freshwater sources dominate across the whole region.[182] In the atmosphere, OH is the most important sink of CH_4 (85% or more[53]) (also see Chapter 6).

The most important natural sources of CH_4 are wetlands, particularly tropical wetlands.[34, 121, 137, 219, 220] Emissions of methane from tropical wetlands contribute 60–80% of global emissions from natural wetlands.[220] Emissions of CH_4 from tropical wetlands are primarily affected by increasing temperatures since the rate of CH_4 production by methanogenic bacteria increases with increasing temperature,[148, 163] which represents a positive feedback on global warming. Zhang and coworkers[219] have estimated that, depending on scenarios, feedbacks via emissions of CH_4 by wetlands could add an additional radiative forcing of 0.04 W m^{-2} to 0.19 W m^{-2} to the global mean by the end of the 21st century. In boreal wetlands, emissions of CH_4 are also enhanced during thawing of inundated areas during the cold season (December to May).[219]

Other natural sources of CH_4 include wildfires and biomass burning,[96, 139] fresh waters (lakes and rivers),[9, 182] oxygen minimum zones (OMZs) of marine environments,[40] and thawing of permafrost soils.[9] These sources of CH_4 are also affected by climate change, and by depletion of Antarctic ozone (see Chapter 3). OMZs are increasing because of increasing sea-surface temperature due to global warming and hence reduced O_2 solubility is occurring. In OMZs, methanogenic bacteria are the main source of CH_4.[40]

Global warming is also increasing emissions of CH_4 from permafrost soils owing to increasing thaw of permafrost (section 3.3.3). Release of CH_4 from permafrost is moderated by methanotrophs, which oxidise 20–60% of this methane before emission to the atmosphere.[167] The area of thermokarst lakes in the Arctic has expanded over the past 60 years.[9] The rate of emission of CH_4 from these areas was found to be directly proportional to the amount of soil-derived organic carbon entering the lakes because of the erosion of thawing permafrost.[9] In summer, emissions of CH_4 from freshwater systems have been estimated to represent between 11% and 26% of total emissions from the Arctic.[182] Release of CH_4 has also been shown to occur from the Arctic seabed where DOM and CH_4 are preserved within and beneath the subsea permafrost.[161] Hence, emissions of CH_4 from thawing permafrost soils might fuel a positive feedback process that further reinforces global warming and thawing of permafrost. Effects of CH_4 emissions on future trends in stratospheric ozone depend on regions. Outside the polar regions, the cooling of the stratosphere by water vapor formed via oxidation of CH_4 is expected to result in an increase in total column ozone, while inside the polar regions, increases in stratospheric water vapor favours the formation of polar stratospheric clouds, which facilitate ozone depletion in polar spring[150] (see Chapter 1).

4.3 Nitrogen compounds

The effects of climate change and solar UV radiation on the production of three gases containing nitrogen are assessed here: on nitrous oxide (N_2O), and on nitrogen oxides (NO_x = NO + NO_2).

4.3.1 Nitrous oxide

Nitrous oxide is an important greenhouse gas and its oxidation is the dominant source of stratospheric NO_x, which affects the concentrations of stratospheric ozone through the formation of reactive chlorine reservoirs and other stratospheric processes (see Chapter 1). The contribution of N_2O to radiative forcing of climate between 1750 and 2011 was approximately 10% of that of CO_2 (based on estimated changes in concentration).[128]

In terrestrial ecosystems, N_2 and N_2O can be formed by UV- and microbially-mediated processes. On soil surfaces that are exposed to solar UV radiation, increased microbial transformations, causing release of N_2 and N_2O from decomposing litter, have been reported in modelling[38] and empirical studies.[88, 198] It is likely that the increased availability of carbohydrates from photochemical degradation of lignin may facilitate the process of mineralisation of nitrogen-containing natural organic matter by microbes. Emission of N_2O via microbial processes increases with temperature and heavy precipitation events.[170] The reasons are increased water-filled pore space and faster consumption of O_2 via respiration and thus a larger anaerobic volume soil fraction.[170] In addition, thawing of permafrost soils is an important source of N_2O.[190, 191, 212] Rates of emissions of N_2O per unit area from permafrost peatlands in the Arctic were found to be of similar magnitude as those from tropical forest soils, the largest global N_2O source from terrestrial ecosystems.[190, 191] Natural emissions of N_2O from land are similar to N_2O emissions from anthropogenic activities (mainly agriculture).[41]

In the ocean, N_2O is formed via two pathways, depending on the oxygen concentration.[21, 110] One pathway of formation of N_2O is via nitrification, i.e., microbial oxidation of ammonia (NH_4^+) to nitrate (NO_3^-), where N_2O is an intermediate product. This biotic formation of N_2O involves ammonia-oxidising bacteria and/or *Archaea,* depending on the salinity of marine environments.[124] Nitrification occurs nearly everywhere in the global ocean, where natural organic matter from phytoplankton debris is mineralised, releasing NH_4^+. Hence, marine production of N_2O via nitrification depends on the rates of primary production and re-mineralisation.[21, 110] In the sunlit zone of the ocean, NH_4^+ can also be formed via UV-induced transformation of organic nitrogen-containing compounds from phytoplankton debris.[126, 140]

The second pathway of formation of N_2O in marine environments is de-nitrification; this process occurs in OMZs where concentrations of dissolved O_2 fall below ~160 μg L^{-1}.[110, 185] Emissions of N_2O via de-nitrification are predicted to increase due to expanding OMZs as a result of global warming and resultant decreased O_2 solubility.[110] The trend in emission of N_2O from the global ocean depends on the balance between nitrification and de-nitrification. Based on a global ocean biogeochemical model, Martinez-Rey and coworkers[110] predicted a decrease of 4–12% in emissions of N_2O from 2005 to 2100 from the global ocean due to decreasing primary and export production, and reduced transport of N_2O from the ocean interior to the ocean surface. On the other hand, emissions of N_2O from land are likely to increase, in part due to more frequent and longer lasting heavy precipitation events and enhanced thawing of permafrost in the Arctic.[190, 191, 212]

4.3.2 Nitrogen oxides

The abiotic pathway of NO_x formation from soil and snow surfaces is photolysis of NO_3^- driven by solar UV radiation.[22, 24, 127] In snow, rates of photolysis of NO_3^- increased with the concentrations of sea salt (NaCl)[127] and, due to the attenuation of the incoming UV radiation, decreased with the depth of snow.[24] Hence enhanced snow-melt (section 3.3.3) and thus increased exposure of NO_3^- to solar UV radiation could result in increased emissions of NO_x from snow surfaces. In addition to the UV-induced pathway, NO is produced in soils by microbial nitrification or denitrification, depending on environmental factors such as oxygen- and water-content, temperature, and pH of the soil.[142] In the troposphere, NO_x controls the formation of ground-level ozone and OH, the latter being critically important to the self-cleaning ability of the atmosphere (also see Chapter 6). Furthermore, reactions of NO_2 with OH (during the day) and with O_3 (during the night) yield nitric acid (HNO_3), which undergoes wet deposition and contributes to acid rain.[130]

4.4 Halogen compounds

Interactive effects of solar UV radiation and climate change play an important role in the production and emission of halogen compounds other than CFCs. These "natural" halogen compounds are formed via UV-induced and microbial processes in seawater and on the surface of the cryosphere and are precursors of reactive halogen species that affect tropospheric and stratospheric chemistry. Among the "natural" halocarbons, very short-lived halogenated substances (VSLSs) are important trace gases for stratospheric ozone chemistry.[84, 105, 168, 175, 181] They may reach the lowermost stratosphere, where they are photochemically transformed into reactive halogen species that act as sinks for ozone. VSLSs may account for ~25% of stratospheric bromine and a few per cent of stratospheric chlorine.[84]

In seawater, precursors of reactive halogen species are formed in UV-induced and biological processes. The methyl halides, CH_3Br, CH_3Cl, and CH_3I, are produced through indirect photochemical reactions involving OH.[35, 138] On the other hand, very short-lived brominated halocarbons (BrVSLS), e.g., bromoform ($CHBr_3$), are formed via biotic processes.[84, 105, 168, 175] $CHBr_3$ and dibromomethane CH_2Br_2 are the major BrVSLS (with tropospheric lifetimes of < 6 months) and account for ~80% of the very short-lived organic bromine in the marine boundary layer.[105] The rate of formation of $CHBr_3$ via bromoperoxidase-mediated halogenation of DOM depends on the chemical composition of DOM. Humic acid enhanced the enzyme-mediated production of $CHBr_3$, but amino acids and lignin suppressed production[105] (**Fig. 5**).

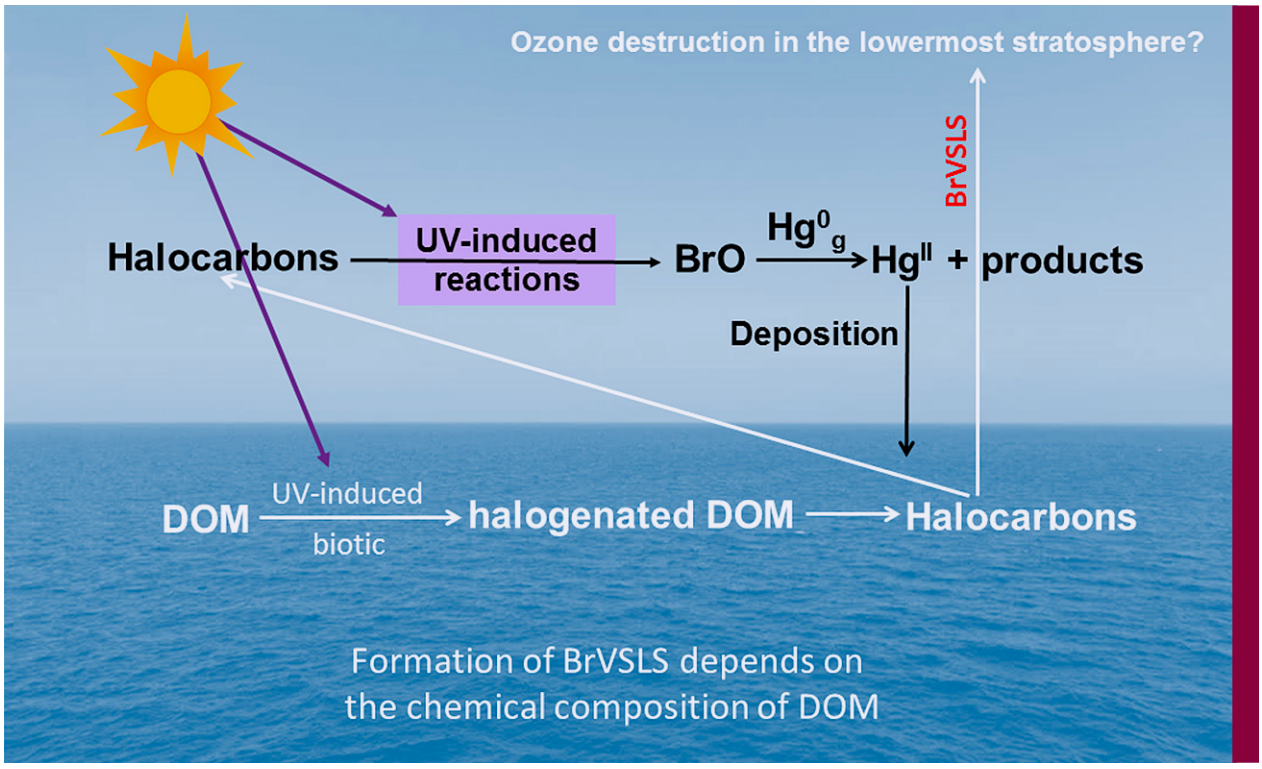

Fig. 5 **Schematic illustration of the formation of halocarbons in seawater that undergo UV-induced reactions in the troposphere yielding reactive halogen species such as BrO that act as oxidants for atmospheric pollutants, e.g., gaseous elementary mercury (Hg^0g). Brominated very-short-lived halocarbons may reach the lowermost stratosphere and participate in stratospheric ozone depletion.**

Ozone depletion potential (ODP)-weighted emissions of $CHBr_3$ (global mean, simulated for 2005) was estimated to account for up to 50% of ODP-weighted anthropogenic emissions of CFC-11.[181] Furthermore, results from simulations suggested that, in 2011, depletion of stratospheric ozone from BrVSLS had a radiative effect that was nearly half that from long-lived halocarbons.[84] The question arises, whether emissions of BrVSLS from natural sources are one reason for the findings that ozone in the lower stratosphere between 60° S and 60° N has continued to decline since 1998.[18]

The extent to which halocarbons reach the lowermost stratosphere depends on their lifetime, and in turn on the concentration of OH in the troposphere, at least for those halocarbons that react with OH, e.g., CH_2Br_2. Rex and coworkers[151] found a coincidence of an "OH minimum zone" over the West Pacific and a relatively long lifetime of CH_2Br_2. Inside the "OH minimum zone" the lifetime of CH_2Br_2 was 188 days at 500 hPa, whereas outside this zone, the CH_2Br_2 lifetime was only 55 days.

In the troposphere, reactive halogen species react with other trace gases such as nitrogen oxides (NO_x),[54, 55] methane (CH_4),[54] ozone,[55, 105] and with mercury.[42, 55, 94] Hence reactive halogen species affect the lifetime of tropospheric pollutants. Reaction of Br with O_3 is thought to be responsible for the episodic decline in the concentrations of ozone to near-zero levels in the lower troposphere over the Arctic, following the boreal springtime polar sunrise.[147] An important pathway for the formation of Br and Cl in the troposphere is photolysis of molecular chlorine and bromine (Cl_2 and Br_2, respectively). This process has been shown to occur in the interstitial air of Arctic surface snowpack.[55, 147]

Bromine monoxide (BrO) is the main atmospheric oxidant of gaseous, elemental mercury (GEM, Hg^0g), which is emitted by human activities.[42] Oxidation of GEM by BrO yields HgII, which is water soluble and, therefore, available for wet deposition.[94] In the marine boundary layer of the Southern Ocean, GEM concentrations ranged from 0.4 to 1.9 ng m^{-3} in Austral summer.[196] Following deposition to aquatic and terrestrial ecosystems, HgII undergoes methylation yielding methylmercury (MeHg), the form of mercury that enters the food web and is highly toxic (**Fig. 5**, also see Chapter 4).

5 Effects of stratospheric ozone and climate change on UV-induced transformations of contaminants

The previous two sections describe how changes in solar radiation affect carbon cycling and emissions of trace gases, biogeochemical processes that have environmental consequences across large geographical and temporal scales. In this section, we consider effects of solar radiation on biogeochemical processes that, while often more localised, may have more direct consequences for the health of humans and other organisms by altering the environmental fate of toxic chemicals and other contaminants. Many processes that drive carbon cycling, such as reactions involving ROS (**Fig. 3**), also apply to contaminants. In addition, human activities that occur simultaneously with contaminant release, such as runoff of nitrogen fertilisers, animal or human wastewaters, and oil spills, contribute photosensitising substances that accelerate photoreactions of contaminants. Contaminants are diverse in their origins and may be commercially-produced chemicals intentionally or accidentally released into the environment (section 5.1.1, and Chapters 4, 6, and 7). In other cases, such as toxins produced by blue-green algae (cyanobacteria), the toxins are a natural component

of ecosystems, but their abundance is increasing because of human activities (section 5.1.2). Contaminants are also highly diverse in their chemistry and responses to solar radiation. UV-B exposure induces direct photoreactions of a wide array of chemical contaminants and initiates free radical processes that oxidise plastics and other commercial products (hence the widespread practice of adding UV-protective substances to prolong lifetimes of plastic, see Chapter 7). Direct photoreactions initiated by the absorption of UV-B radiation by endogenous chromophores may also be the primary mechanism of photodamage in many organisms, for example some pathogenic viruses.[129] For other contaminants, photodamage may involve a much greater element of indirect damage induced by photosensitisers such as CDOM and driven by UV-A and visible wavelengths (400–700 nm) as well as UV-B wavelengths.

The degradation of contaminants in aquatic ecosystems will be assessed although solar UV and visible radiation also plays an important role in the phototransformation of contaminants in the troposphere (see Chapter 6) and on surfaces (e.g., on leaves of plants and surfaces of soils).[63, 109] Modelling of the fate of contaminants, including both direct and indirect photoreactions will be evaluated. Contaminant modelling has primarily focused on the aquatic environment, although photoreactions are important reactions that determine the fate of contaminants such as pesticides in terrestrial ecosystems.

5.1 Degradation of contaminants via direct and indirect photoreactions

Direct photoreactions (Box 1) are the simplest mechanisms for photodegradation of contaminants. The rate of photolysis of a contaminant is directly proportional to its concentration; that is, the reaction is described by a first order rate expression. In indirect photoreactions (Box 2), it is not a contaminant itself that absorbs solar radiation but a photosensitiser. In aquatic ecosystems, important photosensitisers are CDOM, nitrate, and iron compounds (**Fig. 6**). Absorption of solar radiation by a photosensitiser and subsequent reactions produce reactive transients (i.e., short-lived reactive species). These include triplet CDOM (^{3}CDOM*) as well as reactive oxygen species (ROS) such as the hydroxyl radical (OH), superoxide ($O_2^{\cdot-}$), hydrogen peroxide (H_2O_2), and singlet oxygen ($^1O_2$) (**Fig. 3**). These reactive transient species react with a contaminant to form one or more products (Box 2).

CDOM plays a double role in the photodegradation of contaminants. On the one hand, CDOM acts as a photosensitiser for contaminants that are degraded or inactivated via indirect photoreactions. On the other hand,

Box 1 Direct photoreaction

Solar radiation is absorbed by a molecule C (including biological molecules within organisms), e.g., a contaminant, followed by reaction of C* to form breakdown product(s).

$$C \xrightarrow{UV} C^* \rightarrow \text{breakdown product(s)}$$

(C is the molecule being degraded and C* is Photo-excited C.)

Box 2 Indirect photoreaction

A molecule C, e.g. a contaminant, is transformed by reaction with short-lived reactive transients that are produced in photochemical reactions of other light-absorbing substance (known as "photosensitiser", S). These transients include reactive oxygen species (ROS) but are not limited to ROS.

$$S \xrightarrow{UV} S^* \rightarrow \textit{transient species}$$
$$C + \textit{transient species} \rightarrow \text{product(s)}$$

(C is the molecule being degraded, S is the photosensitiser, S* is photo-excited S.)

CDOM protects contaminants that undergo direct photodegradation from UV-B radiation (**Fig. 6**). Increasing runoff of CDOM due to thawing of permafrost, and heavy precipitation events, so-called browning of aquatic ecosystems[205] (see Chapter 4), is likely to enhance indirect photoreactions via several mechanisms. Production of reactive transient species with CDOM acting as the photosensitiser partly offsets the decreases in direct photodegradation rates caused by concurrent protection against UV radiation. Another effect of CDOM acting as the photosensitiser is to shift the photodegradation of contaminants to a greater dependence on UV-A radiation, which penetrates to greater depths in the water column, and hence to a greater dependence on the dynamics of vertical mixing. Droughts would have the opposite effect, i.e., direct photoreactions driven by UV-B radiation would be expected to be predominant because of decreased runoff and thus smaller CDOM concentrations in aquatic ecosystems.

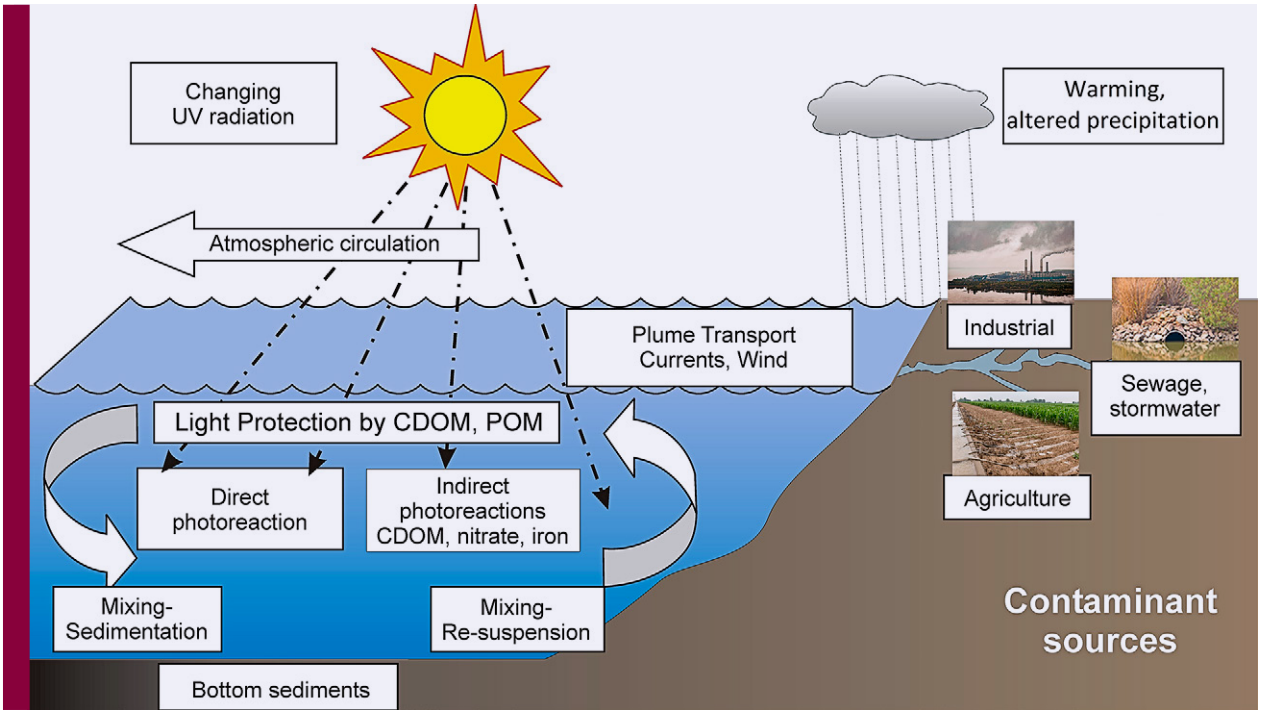

Fig. 6 **Schematic illustrating processes that affect photoreactions of contaminants in aquatic environments. The two main pathways, direct and indirect photoreactions, are described in Box 1 and Box 2 above.**

The predicted decline in UV-B radiation in many areas of the Earth due to recovery of stratospheric ozone (see Chapter 1) is expected to reduce the rate of direct photodegradation or photoinactivation since light-absorbing contaminants are particularly susceptible to being broken down by UV-B radiation. One key indicator of dependence of photoprocesses on UV-B radiation is its radiation amplification factor (RAF, see ref.[118]). RAFs were originally developed as a measure of the sensitivity of a photoprocess to stratospheric ozone depletion.[118] Since they depend on the balance between the effects of shorter (UV-B) and longer wavelengths, with higher RAFs indicating a greater dependence on UV-B radiation, they have much wider application. RAFs for endogenous inactivation of some coliphages[216] (viruses used as indicators of biological contamination) are similar to the RAF (1.0–1.1) for the UV index (UVI) used to quantify damaging UV radiation in human skin (see Chapter 1). The RAFs for

direct photodegradation of chemical contaminants can be of the same order. The RAFs for indirect photoprocesses involving CDOM are typically much smaller (~0.3) than for the UVI, reflecting the greater role of longer wavelength radiation than that of direct photodamage. However, some indirect processes involving inorganic sensitisers in natural waters can be closer to the UVI RAF, for example the RAF for nitrate-sensitised indirect processes is ~0.6. These different wavelength responses, reflected in this range of RAFs, mean that the balance between different mechanisms contributing to photochemical changes is expected to vary with multiple elements of global change.

Examples of the extensive work on interactions of UV radiation with chemical and biological contaminants are provided in **Table 1**, which shows the broad scope of effects that solar UV radiation has on contaminants and that both direct and indirect photoreactions drive the degradation of contaminants. The examples are subdivided according to their susceptibility to direct or indirect photoreactions. However, for many contaminants, both direct and indirect processes are involved, e.g. photoreactions of the lampricides, TFM and niclosamide.[115, 116] In the last four years there has been a growing realisation of the importance of indirect photoreactions in the environment. This change in perception has partly stemmed from more studies focusing on this photoprocess but also because future projections suggest that the indirect mechanism for degradation of contaminants will increase with environmental change. Triplet state intermediates of CDOM often mediate indirect photoreactions.[119] Recent research has shown that chemicals such as "persistent organic pollutants", thought once to be resistant to biodegradation and photodegradation, can be transformed by indirect pathways.[75, 119, 154] Indirect photoreactions are often initiated by CDOM, but inorganic substances such as nitrate, hydrogen peroxide, and iron/peroxides (photo-Fenton) can also sensitise photoreactions.[187] The pathway of phototransformation of contaminants (via direct and/or indirect photoreactions) may influence the "toxicity" of byproducts formed in these photochemical processes. For example, antibiotics usually undergo indirect photoreactions (see **Table 1**). In general, indirect photochemical transformations preserve the basic chemical structure or backbone of an antibiotic, which means that many of the by-products of phototransformation have similar antibacterial properties as the original antibiotics. As a consequence, bacterial resistance of antibiotics could be extended from the point where they enter aquatic ecosystems to coastal areas.[71]

Table 1 **Schematic showing examples of contaminants that are transformed via direct and/or indirect photochemical reactions (photoreactions). Changes in UV radiation, linked to changes in stratospheric ozone, as well as climate, modulate the balance between direct and indirect photoreactions.**

Direct photoreactions	Both	Indirect photoreactions
PHOTOSENSITIVE PESTICIDES **UV-B induced, direct photoreactions dominate. UV-absorbing films can be used to reduce rates of photodegradation.**[3, 203]	**ORGANOPHOSPHORO-THIONATE PESTICIDES** **Fenitrothion undergoes direct photodegradation while diazinon is degraded by the indirect, nitrate-sensitised pathway.**[187]	**POPs[a], PBDEs[a], AND OTHER BIOREFRACTORY CHEMICALS** **Susceptible to indirect photoreactions.**[75, 119, 154]
CARBONYL COMPOUNDS (especially AROMATIC KETONES) **Absorb in the UV-B region; triplet states participate in H-atom abstraction and electron transfer and also initiate indirect photoreactions.**[119]	**ANTIBIOTICS** **Direct pathway is dominant for Cipro and indirect pathway for others.**[107]	**ANTIBIOTICS** **Indirect pathway is usually dominant.**[107, 119]

[a] POPs, Persistent Organic Pollutants; PBDEs, Polybrominated Diphenyl Ethers.

Direct photoreactions	Both	Indirect photoreactions
	LAMPRICIDE **Direct and indirect photo-reactions influence fate.**[115, 116]	**NANOSILVER** **CDOM-sensitised photo-reactions reduce ionic silver to nanosilver.**[85]
	GRAPHENE OXIDE **See refs.**[85, 86]	**UV FILTERS** **Only indirect photoreactions are important.**[160]
	OIL SPILLS **Combination of indirect and direct photodegradation at surfaces, coupled with photofacilitated biodegradation.**[79, 201]	**MICROPLASTICS** **Are produced by indirect photoreactions**[6] **(also see Chapter 7).**
	PATHOGENIC BACTERIA, VIRUSES, AND PROTOZOANS **Undergo direct (endogenous) and indirect (exogenous) photoinactivation**[129] **(see Fig. 8).**	

[a] POPs, Persistent Organic Pollutants; PBDEs, Polybrominated Diphenyl Ethers.

5.1.1 Organic contaminants, nanomaterials, microplastics, and oil spills

Organic contaminants are man-made chemicals including pesticides, pharmaceuticals, household and industrial products, fuels and other petrochemicals, nanomaterials, and microplastics. In some cases, exposure to UV radiation partially transforms contaminants to more toxic substances, e.g., conversion of graphene oxide to polycyclic hydrocarbons.[86]

Engineered nanomaterials (ENMs) are commonly incorporated as fillers in composites with plastics to improve their mechanical properties, conductivity, thermal stability, flame retardancy and other properties. Some of the resulting plastic nanocomposites are quite stable and likely to be very persistent in the environment. UV-initiated photoreactions play a key role in the release of nanomaterials from polymer composites by inducing weathering of the plastic matrix. The degradation of the polymer matrix is particularly important in this release.[208, 209] Exposure to UV radiation also plays a role in the weathering of macroplastics to microplastics (1 nm to 5 mm in size), which are widespread contaminants of freshwaters and oceans[6] (also see Chapter 7). Although plastic nanocomposites have not been shown to similarly form nano-containing microplastics, it is likely that the more persistent nanocomposites may be transported and transformed in a similar fashion. Two papers[78, 82] have provided overviews of chemical additives present in plastics, including their migration, release, fate and environmental impact during use, disposal, and recycling.

Oil spills result in accumulation of contamination on the water surface where full exposure to solar UV radiation occurs. One example was the Deepwater Horizon oil spill of 2010 where extensive amounts of oil floated on the surface of the Gulf of Mexico for over 100 days. Recent evidence[201] has demonstrated that photo-oxidation by sunlight largely accounted for the oxidation of the surface oil (**Fig. 7**), but it was not possible to fully assess the chemical composition and toxicity of the photo-oxidised residues of the oil spill. However, their study, coupled with another study[79] showed that photo-oxidation of the oil and its partially-oxidised residues on beach sands photo-facilitated its microbial degradation by increasing

the carbonyl content (**Fig. 7**), another previously overlooked effect of photo-oxidation on dissipation of oil spills.

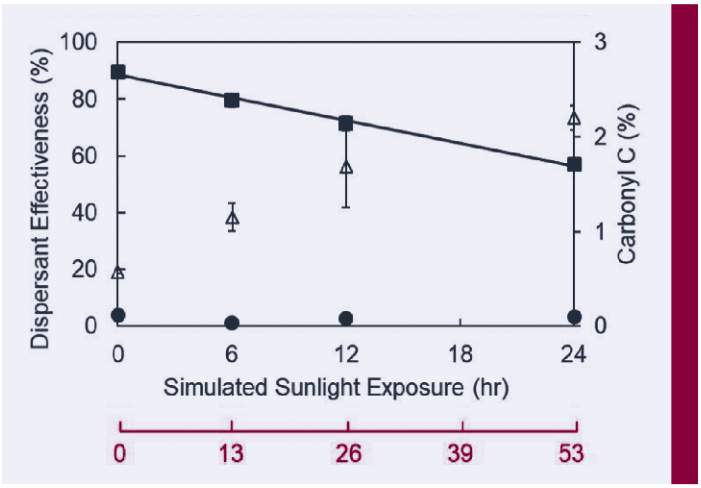

Fig. 7 **As oil is increasingly exposed to sunlight, its carbonyl content (Δ) increases, indicative of partial photo-oxidation of hydrocarbons in the oil to form oxidised organic compounds. This change in chemical composition of the oil decreases its chemical dispersion (■) (without much change in its natural dispersion (●)). See ref.[200] for more information. (Reproduced with permission of the American Chemical Society (ACS) from Fig. 1 of ref.[201], https://pubs.acs.org/doi/abs/10.1021%2Facs.estlett.8b00084. Permission related to the material excerpted should be directed to the ACS).**

5.1.2 Harmful algal blooms and other biological contaminants

Eutrophication of freshwater and coastal ecosystems causes harmful algal blooms, particularly with cyanobacteria, which are a pervasive global threat to ecosystems and human health. In large temperate lakes, harmful algal blooms are often dominated by *Microcystis* species that produce potent neurotoxins, threaten drinking water supplies, and stimulate autotrophic carbon production and subsequent hypoxia.

In recent years, Lake Erie has experienced two of the largest recorded blooms in its history. In 2011, 2013, 2014, and in 2015 elevated concentrations of the neurotoxin microcystins shut down the drinking water supply to nearly a half million people.[120]

Key drivers such as temperature and nutrients alone or together do not fully explain patterns of the occurrence or toxicity of harmful algal blooms (e.g., ref.[174]). Recently, it has been suggested that photochemical processes driven by CDOM may mitigate the toxicity of harmful algal blooms.[135] On the one hand, hydrogen peroxide (H_2O_2) produced by photochemical reactions of CDOM may be less damaging to toxic strains of *Microcystis* than non-toxic strains.[58, 221] Recent work has shown that high concentrations of H_2O_2 in Lake Erie are associated with toxic strains of *Microcystis*, while non-toxic strains were dominant when H_2O_2 concentrations were lower[25, 45] On the other hand, photochemical reactions of CDOM may promote the degradation of algal toxins.[27] Understanding the balance of these light-mediated effects of CDOM on *Microcystis* and its toxins is important because concentrations of dissolved organic matter (and thus CDOM) are increasing in North American and European freshwaters[205] (see Chapter 4).

Harmful algal blooms are not the only health-related microorganisms strongly affected by exposure to solar radiation. Exposure to solar UV radiation in the environment inactivates or kills many viruses, bacteria and other microbes that cause water-borne diseases in humans and other animals[129] (also see Chapters 2 and 4). As with chemical contaminants (**Table 1**), pathogenic micro-organisms may be damaged by direct and/or indirect photoreactions, also referred to as endogenous and exogenous inactivation, respectively.[129] Recent advances in the understanding and modelling of microbial responses to solar radiation[129, 205] provide a

broad conceptual framework for assessing the responses of contaminants to sunlight, and how those responses may alter given expected changes in stratospheric ozone, climate and other components of global change (section 5.3).

5.2 Modelling of photodegradation or photoinactivation of contaminants

Advances in modeling approaches are allowing improved quantification of effects of global changes on the fate of synthetic and biological contaminants. Modeling is also used to assist with the design of treatment processes that rely on solar disinfection. Many contaminants are degraded via both direct and indirect photoreactions (**Table 1**). An important metric for characterizing the fate of contaminants is their half-life ($t_{1/2}$, i.e., the time taken for degradation to half of the initial concentration) in a given environmental system. This half-life is calculated from Eq. 1,

$$t_{1/2} = \ln 2 / k_{tot} \quad (1)$$

where k_{tot} is the first-order rate constant of photodegradation or photoinactivation of contaminants and can be modeled including direct and indirect photoreactions ($k_{tot} = k_{dir} + k_{indir}$).

5.2.1 Modelling of direct photoreactions

The first-order rate constant of direct photochemical reactions, kdir, depends on the specific rate of light absorption by the contaminant, k_a, as well as on the reaction quantum yield (Φ) (Eq. 2).

$$k_{dir} = k_a \times \Phi \quad (2)$$

The quantum yield is the fraction of absorbed light that results in photoreaction. The specific rate of light absorption, k_a, is a measure of the spectral overlap of the solar spectral irradiance and the absorption spectrum of the contaminant and is sensitive to changes in the absorption spectra of the contaminants, climate, and stratospheric ozone. The reasons for this sensitivity are that solar spectral irradiance that strikes the surface of a water body, particularly in the UV-B range, depends on concentrations of stratospheric ozone as well as on cloud cover and concentrations and composition of aerosols. Decreased atmospheric ozone in recent decades will have tended to increase rates of UV-B-induced photoreactions of contaminant, primarily direct photoreactions of the type described in the left column of **Table 1**. As the stratospheric ozone layer recovers (see Chapter 1), UV-B radiation will decline in many areas. Assuming this effect would be approximated by estimated changes in UVI, as seems reasonable given the relevant RAFs, this change in ozone would reduce these UV-B photoreactions by up to 5–15%. The effect of stratospheric ozone recovery would be much smaller for indirect photoreactions, given their smaller RAFs.

As discussed above, CDOM is the main light-absorbing compound in many aquatic ecosystems. Therefore, k_a depends not only on the extinction coefficient (absorption properties) of a considered contaminant but also on the concentration and absorption properties of CDOM and of all other light-absorbing materials present in a water body, including POM. Hence the specific rate of light absorption by a contaminant, k_a, and thus the first-order rate constant of a direct photochemical reaction decreases exponentially with increasing depth of a water body, and with increasing concentration and absorption of solar radiation by

CDOM and other light-absorbing components contained in aquatic ecosystems. Simulations of photodegradation of contaminants via direct photoreactions require estimates of the solar spectral irradiance, principally the UV irradiance that strikes the surface of a water body. Mathematical models have been developed to quantify photolysis of contaminants in different aquatic environments and at different solar zenith angles (a function of latitude, time of year and time of day).[29, 99, 129, 131, 216]

5.2.2 Modelling of indirect photoreactions

The first-order rate constant of indirect photochemical reactions, k_{indir}, depends on the steady-state concentration of a reactive transient species ($[RT_i]_{ss}$) and on the second-order rate constant of reaction of a reactive transient species with a contaminant (k_i). The photochemical production of reactive transients involving photosensitisers occurs far into the UV-A and visible region. In aquatic ecosystems, many reactive transients are present and, therefore, indirect photoreactions of contaminants have been quantified by summing individual rate expressions for reaction of a contaminant with each of several reactive transients produced by sunlight in the water (Eq. 3).

$$k_{indir} = \Sigma k_i [RT_i]_{ss} \quad (3)$$

The assessment of kindir requires experiments that define the second-order rate constant, k_i, for reaction of the contaminant with each transient. An alternative approach is to use action spectra, i.e., weighting functions, in the calculations of second-order rate constants.[123, 129, 131, 164, 165, 216] The use of action spectra has been employed mainly to estimate second-order rate constants for biological contaminants. The steady-state concentrations of transients, $[RT_i]_{ss}$, can be directly measured[16, 86, 97, 111, 123] or simulated.[29, 16, 86, 97, 99, 111, 123]

5.3 A conceptual framework for assessing changes in the photo-biogeochemistry of contaminants in response to changes in stratospheric ozone and other components of global change

As noted in the Introduction, future changes in exposure to solar UV radiation are likely to be affected not just by changes in stratospheric ozone but by other factors including cloud, aerosols, surface reflectivity coupled with ice/snow loss (see Chapter 1), and changes in the concentration of CDOM in water bodies[205] (see Chapter 4). While changes in stratospheric ozone preferentially affect UV-B radiation, changes in these other factors will also affect UV-A radiation, and even wavelengths greater than 400 nm (see Chapter 1). These more heterogeneous changes will affect rates of photochemical processes as well as the balance between direct and indirect photochemistry. The concentration of CDOM in a water body is critical. On the one hand, by attenuating solar radiation, particularly UV radiation, CDOM protects synthetic and biological contaminants that undergo direct photoreactions. On the other hand, CDOM acts as a photosensitiser and, therefore, enables indirect photoreactions. Thus, the balance between different mechanisms by which contaminants are transformed or inactivated depends on their susceptibility to direct or indirect photoreactions (**Table 1**), on the depth in a water body, and on environmental factors such as the concentration and absorption properties of CDOM. These potentially complex interactions have been considered in a case study.[129] This study investigated the role of sunlight in the inactivation of two

different viruses at different depths in a water column containing CDOM, which acted as an exogenous photosensitiser in indirect photoinactivation. They modeled the total rate constant, k_{tot}, of photoinactivation as the sum of three mechanisms

(i) Light-independent (dark) mechanisms

(ii) Direct light-dependent mechanisms

(iii) Indirect light-dependent mechanisms

They compared the effect of depth in the water column on k_{tot} of photoinactivation of two viruses, poliovirus, and the phage MS2, using the model parameters from ref.[166] for a wetland during the month of June in Northern California. Poliovirus undergoes mainly direct photoinactivation, whereas MS2 is mainly inactivated by photosensitised processes (green and brown areas, respectively, in the right panel of **Fig. 8**).

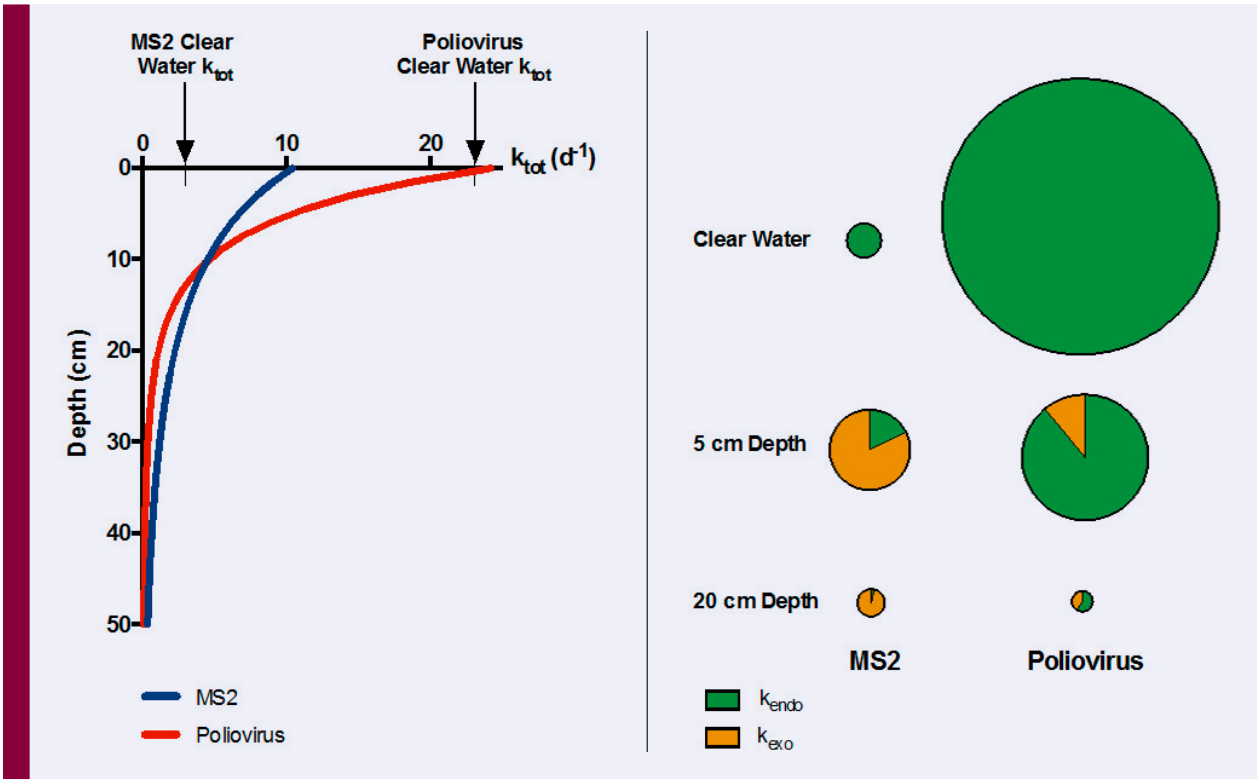

Fig. 8 **Modelled depth dependence of the rate constant k_{tot} of photoinactivation of MS2 coliphage and poliovirus in a water body with the same optical properties and exogenous photosensitiser concentrations as observed in a simulated open water wetland.[129] The term "clear water" indicates that k_{tot} was computed assuming water at the surface with no light attenuation or sensitisation by CDOM. k_{endo} and k_{exo} are the first-order rate constants for direct and indirect photoinactivation, respectively. The circles in the right panel represent k_{tot} and include both direct (green) and indirect (brown) photoinactivation ($k_{tot} = k_{endo} + k_{exo}$). The abbreviations "endo" and "exo" refer to the light-absorbing compounds, i.e., biological molecules inside the viruses and CDOM outside the viruses, respectively. (Reproduced with permission of the Royal Society of Chemistry from Fig 10 of ref.[129]).**

At the surface of clear water, k_{tot} of photoinactivation of poliovirus is 20 times greater than k_{tot} of MS2 photoinactivation (right panel in **Fig. 8**). By contrast, at the surface of simulated wetland water containing CDOM, k_{tot} of poliovirus photoinactivation is only 2.5 times greater than k_{tot} of MS2 photoinactivation (left panel in **Fig. 8**). This contrast is due to CDOM acting as a photosensitiser in the simulated wetland water and hence k_{tot} of MS2 photoinactivation is greater than in water without CDOM. At 5-cm depth in water containing CDOM, k_{tot} for MS2 is greater than in clear water since MS2 is mainly susceptible to indirect photoinactivation, whereas k_{tot} for poliovirus is smaller than in clear water, due to the attenuation of UV-B radiation by CDOM. At depths greater than 11 cm, MS2 receives greater photodamage than poliovirus (left panel in **Fig. 8**) since k_{endo} decreases more strongly with depth than k_{exo}. This phenomenon is due to the fast attenuation of the damaging solar UV-B radiation with depth, while deeper penetrating longer wavelengths are involved in the photoproduction of reactive transients, and hence indirect photoinactivation. This is also shown in the right panel of **Fig. 8**, where k_{tot} for MS2 is greater than k_{tot} for poliovirus at 20 cm depth. If the water column containing CDOM would be well mixed to about 50 cm depth, k_{tot} averaged over the full depth of the column would be approximately equal for MS2 and poliovirus.

The complex interplay of direct and indirect mechanisms with different wavelength dependencies, absorption properties of any dissolved or suspended material, and the extent of mixing can lead to patterns of photodamage not evident from the responses of organisms measured in clear water, including measurements made under typical laboratory conditions. Since indirect photoreactions mediated by CDOM are affected by wavelengths well into the UV-A and visible region they have much lower sensitivity to changes in ozone and much deeper penetration into water bodies in general. Considering the large effect of CDOM on the inactivation rate constants even with a change in depth of a few cm, we hypothesise that ozone-related changes are much smaller than changes caused by CDOM, even for direct photodegradation. Hence, increases in runoff of CDOM, so-called browning,[206] could affect contaminant degradation rates much more substantially in the future than the small changes projected for ozone increases. Conversely, decreases in CDOM related to drought and reduced runoff could result in much larger increases in UV-related contaminant photodegradation than observed or projected ozone changes. Results similar to poliovirus can be demonstrated for direct photoinactivation of coliphage phiX174 by solar UV-B radiation in beach waters of the Great Lakes; like poliovirus, phiX174 photoreacts predominately by the UV-B-induced direct mechanism.[216]

Given the parallels in the balance of direct and indirect photoprocesses between micro-organisms and chemical contaminants **(Table 1)**, we suggest that the results shown in **Fig. 8** can be generalised to include chemical contaminants. For example, photoreaction of the antibiotic ciprofloxin proceeds exclusively by UV-B-induced direct photoreaction, and so its responses may be close to those of poliovirus, whereas other antibiotics photoreact by indirect pathways mediated by CDOM, and so are closer to MS2.[107] Likewise, UV-B radiation induces direct photoreaction of the organophosphorus insecticide fenitrothion but diazinon, another organophosphorus insecticide, photoreacts in natural waters by indirect mechanisms that are induced through UV-B radiation absorbed by nitrate ions in the water.[187] In this case, the prediction is that fenitrothion will respond to factors such as the concentration of CDOM and the depth in the water column, similar to the response of poliovirus, while diazinon is expected to be more similar to MS2. The latter findings show that not only CDOM but also inorganic compounds such as nitrate can act as photosensitisers, and in many environments the two may occur together. If nitrate as a photosensitiser had been included in the scenario modelled in **Fig. 8**, then k_{tot} of photoinactivation of MS2 would have been greater at the surface

of the simulated water body but would have dropped off more sharply than shown in **Fig. 8**, i.e., the dependence on depth of k_{tot} for MS2 would be closer to that for poliovirus.

The new modelling techniques as shown in the example above are providing useful insights into the most important mechanisms for contaminant photoreactions and dependence of the rates of these processes on changes in time, location, water depth, and stratospheric ozone concentrations. Other examples apply to chemical contaminants. Photoreactions of contaminants have been modelled in boreal lakes to provide comprehensive maps of indirect and direct photoreactions over a large geographic region of Sweden.[97] In the case of indirect photoreactions, recent and projected future changes in "browning" of the lakes are creating unfavourable environments for indirect photoreactions mediated by OH and carbonate radical anions but increasingly favourable environments for indirect photoreactions involving CDOM triplet states and singlet oxygen. Another modelling study of ocean water in Terra Nova Bay, Antarctica, indicated that two sample contaminants, the solar filter, benzophenone-3, and antimicrobial agent, triclosan, would have photochemical half-lives of less than a few days during the Antarctic summer due to indirect photoreactions primarily mediated by CDOM triplet states.[123] Other modelling studies in four Alpine lakes of Europe predict that indirect photoreactions in the lakes may be significantly altered by future changes in water alkalinity and dissolved organic carbon caused by climate change.[122]

6 Feedbacks on global warming that are mediated by UV and visible radiation

The effects of changes in ozone and climate on biogeochemical cycles that are mediated by solar UV and visible radiation have the potential to drive feedbacks to global warming (**Fig. 9**), although critical gaps in knowledge (section 7) makes it difficult to quantify the magnitude of any such feedbacks. Droughts can increase exposure of dead plant material (litter) to solar radiation due to the reduction in plant cover. Hence the photochemical decomposition of litter can be accelerated, yielding increased emissions of CO_2 to the atmosphere and organic compounds that can be more easily degraded by microorganisms (photofacilitation), increasing microbial respiration.

Wildfires, because of droughts, are direct sources of CO_2 and other greenhouse gases, particularly CH_4. In addition, wildfires transform NOM into compounds that are more susceptible to photodegradation, which increases the release of CO_2. Wildfires also enhance the thawing of permafrost soils. Extreme precipitation events (storms in **Fig. 9**) and thawing of permafrost soils enhance the flow of soil organic matter from land to fresh and coastal waters and hence the exposure to solar radiation of particulate and dissolved organic matter from soils (POM and tDOM, respectively). In aquatic ecosystems, POM and tDOM undergo photodegradation in similar ways as in terrestrial ecosystems yielding CO_2 and other products, where photofacilitation plays an important role. The net result of the interactive effects of UV and visible radiation and climate change on carbon cycling are a reduction of carbon storage in soils, and an increased release of CO_2 into the atmosphere, which reinforces climate change (positive feedback).

Climate-change related increases in emissions of greenhouse gases other than CO_2 may also cause positive feedbacks on global warming. Photodegradation of tDOM not only yields CO_2 but also CO and other products. CO competes with CH_4 for OH, where reaction of CH_4 with OH is the major sink of CH_4 in the troposphere. Thus, CO emission from tDOM photodegradation

might fuel a positive feedback on global warming via a longer lifetime of CH_4, an important GHG, in the troposphere. Thawing of permafrost soils due to global warming also enhances emissions of N_2O, another important GHG. Thus, emissions of N_2O from permafrost soils might fuel a positive feedback by reinforcing thawing of permafrost soils.

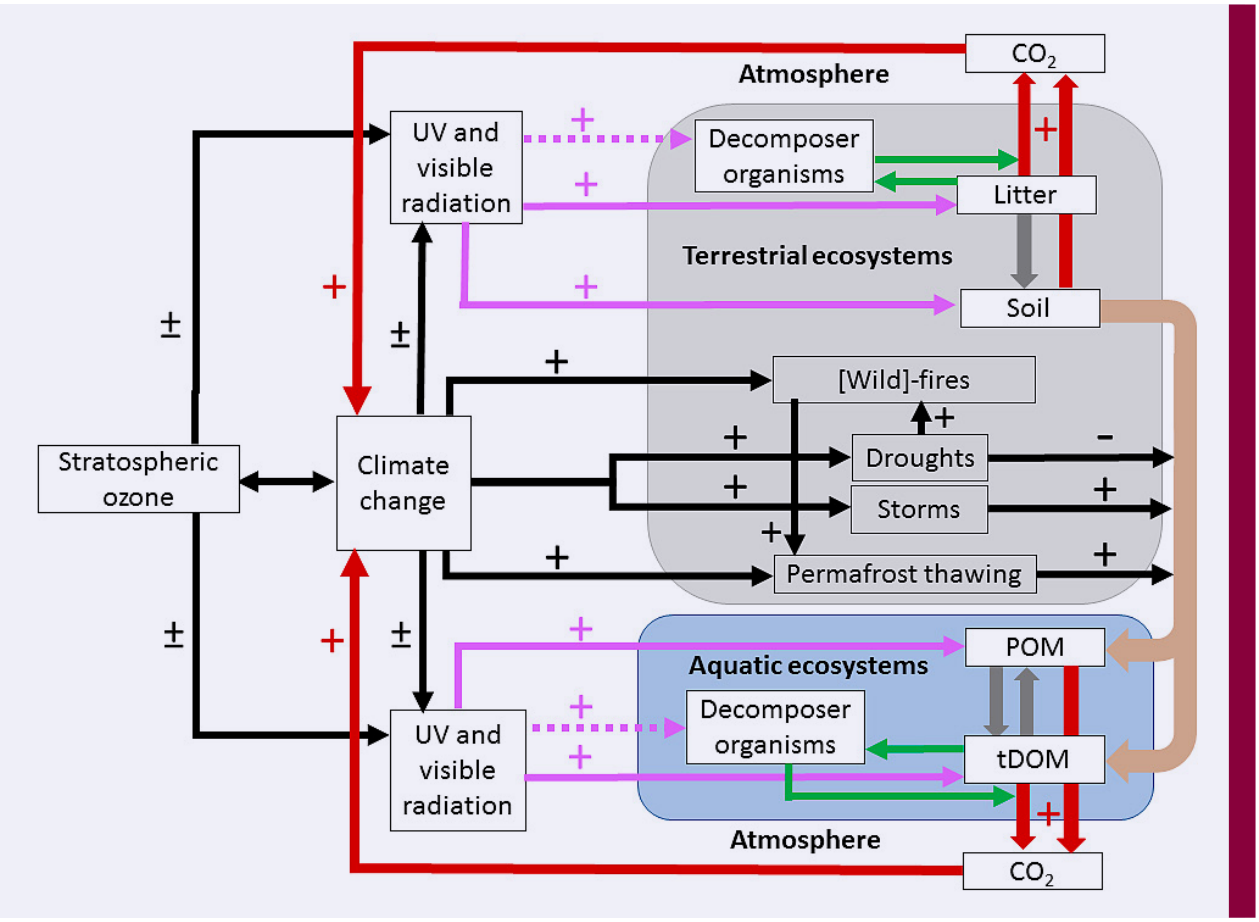

Fig. 9 **Interactive effects of solar radiation and climate change on the flow of natural organic matter (NOM) from soils into aquatic ecosystems (rivers, lakes, coastal waters), and on the photodegradation of NOM on land and in water. Key to symbols: Black arrows indicate interactions between changes in stratospheric ozone, solar UV radiation, and climate and their effects on changes on land (permafrost thawing, storms, droughts, (wild)-fires) that influence the flow of soil organic matter from land to water. Dashed arrows indicate direct effects of solar UV radiation on decomposer organisms (see Chapters 3 and 4). Purple arrows indicate the effects of solar UV and visible radiation on the degradation of soil and litter in terrestrial ecosystems and of POM and tDOM in aquatic ecosystems. Green arrows refer to the process of photofacilitation. Brown arrows indicate the flow of carbon from terrestrial to aquatic ecosystems. Red arrows indicate the release of CO_2 from terrestrial and aquatic ecosystems to the atmosphere and the feedback on climate change. The symbols + and – indicate an enhanced or reduced effect on a change, flow or process.**

7 Major advances and gaps in knowledge

As highlighted in the previous sections, there is increasing awareness that a wide range of biogeochemical processes that are mediated by solar radiation, and so liable to be influenced by changes in stratospheric ozone, may interact with effects of climate change such as the loss of the cryosphere, droughts, and extreme precipitation events. These effects enhance the exposure of NOM to solar radiation and thus the likelihood for photodegradation. The processes involved in the photodegradation of NOM are now better understood and include direct and indirect photoreactions, as well as photofacilitation.

Gaps in knowledge relating to carbon cycling include (1) the net effect of land-use change (including conversions due to agriculture, deforestation, and afforestation) on the photodegradation of plant litter, (2) the role of reactive oxygen species (ROS) and iron in the photodegradation of tDOM in aquatic ecosystems, (3) the relative importance of ROS vs products of tDOM photodegradation on subsequent microbial respiration, (4) the timescales of tDOM photodegradation relative to water residence times and inputs of "fresh" tDOM from land, (5) how rates of tDOM photodegradation will be affected by changes in the ratio of UV and visible radiation reaching surface waters due to changes in ice cover on lakes, cloud cover, wildfire, or changes in stratospheric ozone. Modelling approaches as discussed in section 5.3 for contaminants would greatly help to advance our understanding on these outstanding issues. However, the use of such models is constrained for many biogeochemical processes due to the lack of necessary model inputs. Such inputs might include, for example, a well-defined action spectrum and/or well quantified relationships between the rate of a process and the irradiance or dose of weighted radiation. The progress made in modelling contaminants (see below) provides some encouragement that such gaps could be filled for a wider range of biogeochemical processes.

As for CO_2, effects of climate change may also affect rates of CO production via photodegradation of tDOM (section 4.1) and thus tropospheric concentrations of CH_4, since CO competes with CH_4 for OH. CH_4 and N_2O are greenhouse gases with indirect or direct impacts on stratospheric ozone. Another group of trace gases that affect stratospheric ozone are the brominated very-short-lived substances (BrVSLS). Gaps in knowledge regarding trace gases are: (1) the ratio of CO_2/CO formed via photodegradation of tDOM on a regional and global scale, (2) the reason for the leveling off of tropospheric CH_4 concentrations between 1999–2006, (3) the role of UV and visible radiation in facilitating microbial mineralisation of nitrogen-containing NOM in terrestrial and aquatic ecosystems and thus the release of N_2O, (4) future N_2O emissions from terrestrial and aquatic ecosystems on a global scale, (5) the contribution of BrVSLS emissions from natural sources to ozone depletion in the lower stratosphere.

Since the last Quadrennial Assessment, major advances have been made regarding the biogeochemical cycling of contaminants. Thanks to advanced modelling tools as described in section 5.3, half-lives of contaminants in a given aquatic environment can be predicted for contaminants that are degraded via both direct and indirect photochemical reactions. Gaps in knowledge are: (1) The role of POM in the degradation of contaminants via direct and indirect photoreactions, (2) three-dimensional models that can be used to predict changes in CDOM concentrations and UV radiation, (3) models that can be used to predict UV-induced degradation of contaminants in terrestrial ecosystems, (4) the way in which half-lives of contaminants in a given aquatic ecosystem change with time due to bleaching of CDOM. As noted above, this rapid progress made with contaminants provides an exemplar and

stimulus to develop equally powerful modelling approaches to quantify the role of light-driven processes in large-scale biogeochemistry, above all the carbon cycle.

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6 Interactive effects of changing stratospheric ozone and climate on tropospheric composition, air quality, and the consequences for human and ecosystem health

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Summary

The composition of the air we breathe is determined by emissions, weather, and photochemical transformations induced by solar UV radiation. Photochemical reactions of many emitted chemical compounds can generate important (secondary) pollutants including ground-level ozone (O_3) and some particulate matter, known to be detrimental to human health and ecosystems. Poor air quality is the major environmental cause of premature deaths globally, and even a small decrease in air quality can translate into a large increase in the number of deaths. In many regions of the globe, changes in emissions of pollutants have caused significant changes in air quality. Short-term variability in the weather as well as long-term climatic trends can affect ground-level pollution through several mechanisms. These include large-scale changes in the transport of O_3 from the stratosphere to the troposphere, winds, clouds, and patterns of precipitation. Long-term trends in UV radiation, particularly related to the depletion and recovery of stratospheric ozone, are also expected to result in changes in air quality as well as the self-cleaning capacity of the global atmosphere. The increased use

of substitutes for ozone-depleting substances, in response to the Montreal Protocol, does not currently pose a significant risk to the environment. This includes both the direct emissions of substitutes during use and their atmospheric degradation products (e.g. trifluoroacetic acid, TFA).

1 Introduction

The composition (and the quality) of the air we breathe is critical for life on Earth and is affected by natural and anthropogenic processes throughout the biosphere as well as by solar radiation (**Fig. 1**). In addition to gases, the atmosphere contains many types of particulate matter (PM), that have been both naturally generated (e.g., sea-salt, dust) and anthropogenic (e.g., photochemical smog). These gases and particles circulate in the troposphere (lower atmosphere) and are changed by chemical and physical processes. A key driver of these processes is the amount of UV radiation transmitted through stratospheric ozone (O_3) to the troposphere. Changes in intensity of UV radiation in the troposphere, particularly near the ground, will affect the composition of the atmosphere and change the quality of the air that organisms depend on. These changes can be both harmful and beneficial. For example, UV radiation accelerates the removal of many chemical compounds that are emitted into the atmosphere by human activities. These UV-driven chemical reactions can generate transient products (such as ground level ozone and particulate matter) that degrade air quality before they are removed. Climate change will also affect atmospheric circulation (wind patterns) and will interact with solar radiation to modify the composition of the atmosphere.

Poor air quality has large direct and indirect effects on human health, as well as on terrestrial and aquatic ecosystems. Exposure to polluted air has been associated with a variety of adverse effects in humans; however, identifying associations and causation between effects and a chemical within the mix of gases and particles is difficult.

Adverse effects of poor air quality on the environment include for example, damage to trees other plants, and agriculture, with potentially significant impacts on crop production and hence food security. The effect can also be indirect, whereby air-borne pollutants can change the composition of the soil and water, which can then affect living organisms. Vegetation can, in turn, improve or degrade air quality through multiple complex interactions with the atmosphere.

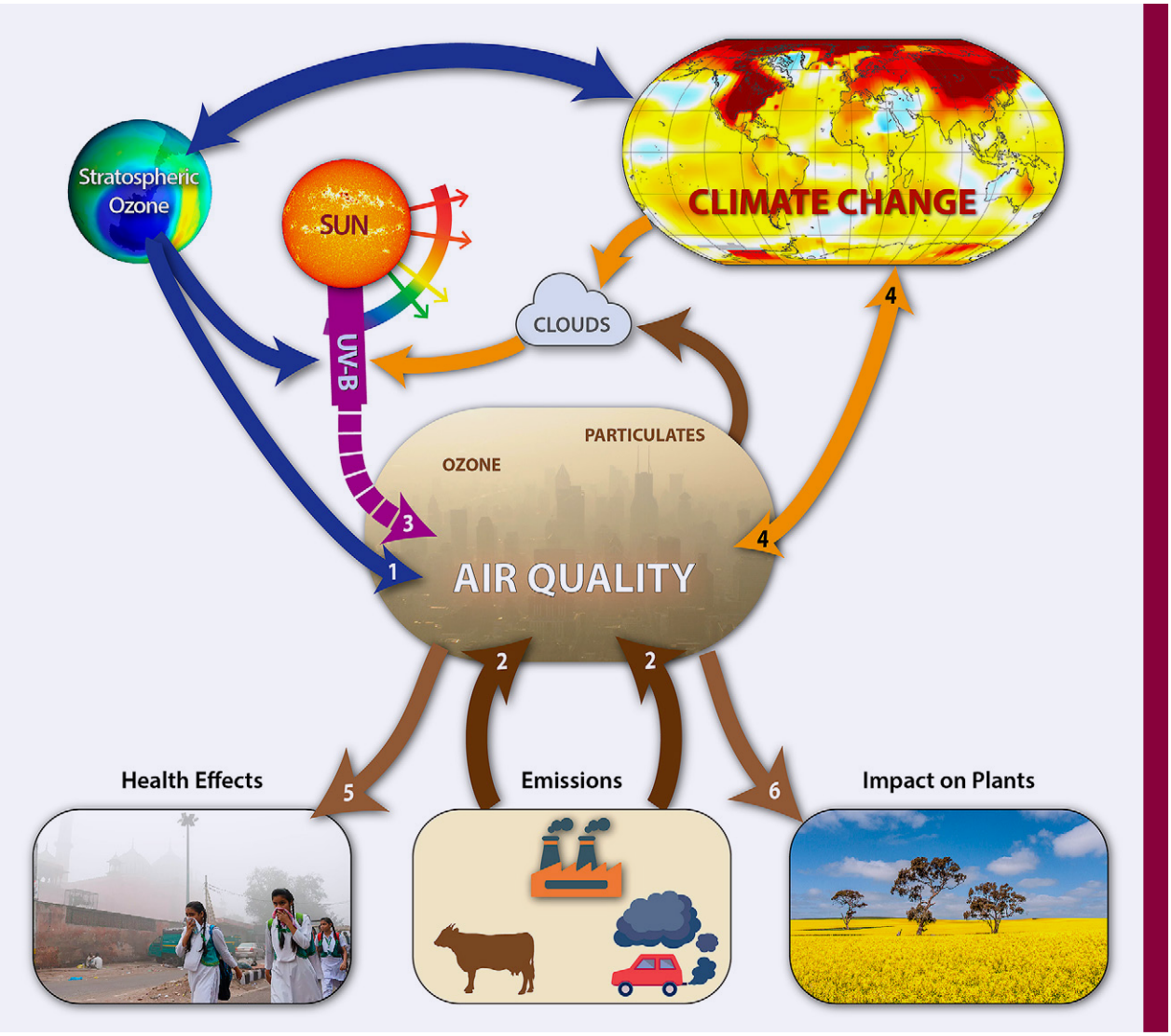

Fig. 1 **Atmospheric composition is determined by the mixture of emissions to the atmosphere, transport within the atmosphere, and UV-B radiation. The key interactions determining the composition includes (1) transport of ozone from the stratosphere, (2) emission of a wide range of substances from the ground, (3) transformation of material through the action of UV radiation (and particularly UV-B), and (4) mixing of the pollutants in the atmosphere. The resultant O_3 and aerosols, in turn, have impacts on human health (5) and plants (6).**

The World Health Organization estimates that poor air quality is now the largest environmental cause of mortality worldwide, exceeding that of poor water quality.[185] An important distinction should be made between the quality of air indoors, and that outdoors for which UV radiation plays a significant role. Poor indoor air quality, coming from sources such as cooking and heating, has long been recognized as a significant concern for human health, and recent estimates suggest that the health impacts of indoor air have declined (**Fig. 2**). Based on the number of deaths globally, the impact of outdoor air pollution on human health has increased. The relationship between concentrations of atmospheric components and human health is widely recognized but quantification is still a matter of significant uncertainty and study.

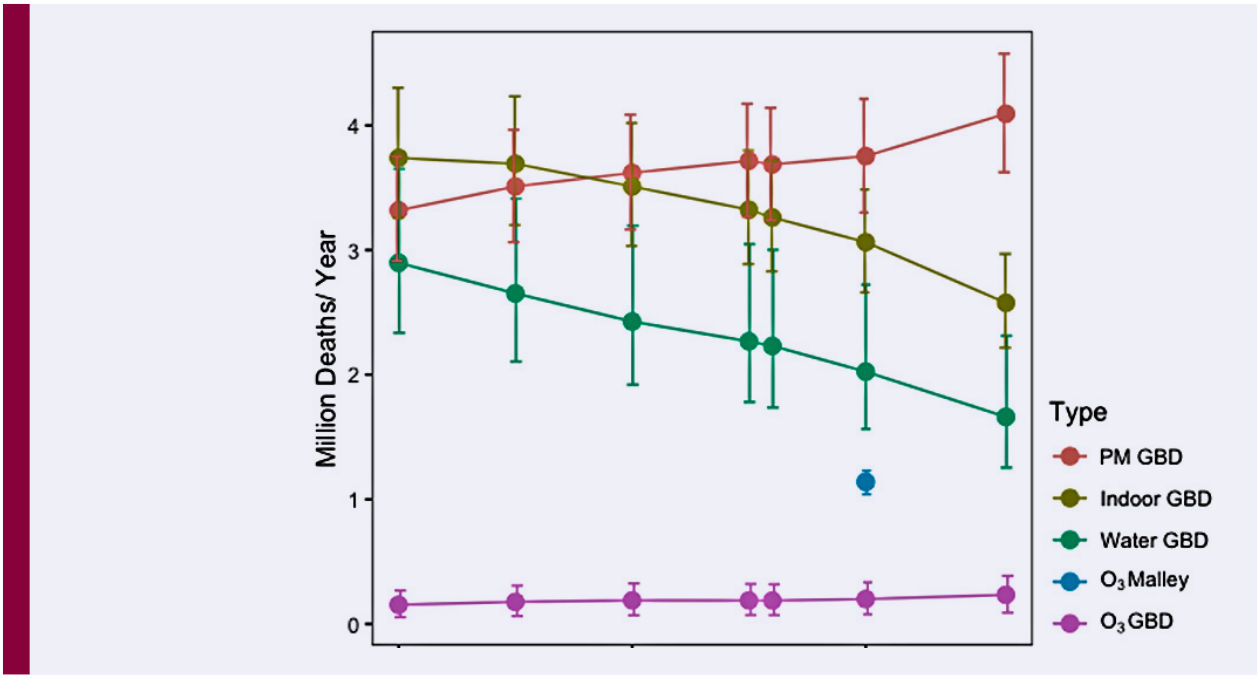

Fig. 2 **Global annual deaths from environmental risk factors. Risk factors shown are primarily from the Global Burden of Disease (GBD) Study (ref.[56]). These are ambient particulate matter (PM) pollution, household air pollution from solid fuels where the major impact is indoors (Indoor), Poor water quality (Water) and ambient ozone pollution (O_3). Also shown is an alternate estimate of deaths from ambient O_3 pollution (O_3 Malley),[119] highlighting the differences in current estimates of human sensitivity to O_3.**

Outdoor air quality is most often defined by key atmospheric components that have a substantial impact (criteria pollutants). For this assessment, the two measures of air quality that will be mainly considered are the ground-level concentrations of O_3 and particulates (more specifically particulate matter smaller than 2.5 micrometers ($PM_{2.5}$)), since both are sensitive to changes in stratospheric O_3 and climate. There are several other criterial pollutants that are important to air quality that will not be considered in detail (such as sulfur and nitrogen oxides).

This assessment is predicated on the understanding that the changes in air quality at a particular location are associated with changes in stratospheric ozone depletion and climate that are driven by three key influences (**Fig. 1**):

1. Chemical changes primarily driven by solar UV radiation, particularly UV-B radiation.
2. Pollutants emitted locally (e.g., by motor vehicles, trees), regionally (e.g., emissions from other cities) or globally (e.g., stratospheric O_3, which is not a pollutant until it is transported to the ground).
3. Atmospheric characteristics, i.e., weather, in terms of temperature, wind (transporting pollutants), rain, and cloudiness, which over longer time frames constitute climate.

The production of surface O_3 by UV-driven photochemistry is illustrated in **Fig. 3** using a simplified reaction scheme. Ozone is produced by the UV-driven photooxidation of hydrocarbons in the presence of nitrogen oxides (NO_x = NO + NO_2). These chemical transformations cause more O_3 to be formed, generate PM, and aid in the final removal of pollutants from the atmosphere. The actual rate of production of O_3 and PM depends on the available amounts of UV radiation, hydrocarbons, and NO_x, and therefore the exposure of humans and vegetation is expected to vary significantly with time and location.

$$O_3 + h\nu\,(\lambda < 330\ \text{nm}) + H_2O \rightarrow 2\,OH + O_2$$

$$RH + OH + O_2 \rightarrow H_2O + RO_2$$

$$RO_2 + NO \rightarrow RO + NO_2$$

$$NO_2 + h\nu\,(\lambda < 420\ \text{nm}) + O_2 \rightarrow NO + O_3$$

Fig. 3 **Generalised reaction scheme for the formation of ground-level ozone (O_3) by UV-driven oxidation of hydrocarbons (RH) in the presence of nitrogen oxides (NO and NO_2). The symbol *hν* represents a photon of wavelength (λ) shorter than the value indicated. Further reactions of RO can lead to organic particulate matter (PM) and additional ozone.**

Here, we assess the changes in air quality due to changes in stratospheric O_3 combined with climate change, emphasizing the new understanding since the last United Nations Environment Program Environmental Effects Assessment Panel quadrennial report.[117] It should be noted that the chemistry in the urban atmosphere can be quite different to that in rural areas.[62] What will not be directly assessed is the effectiveness of regulation, i.e., air quality controls and the relative merits of various air quality standards. However, it is worth noting that substantial progress has been made in controlling avoidable emissions of hydrocarbons from sources like motor vehicles in developed countries (e.g., ref.[123]).

2 Atmospheric circulation and air quality

Physical transport of air masses around the globe is critical for determining air quality for all environments. For air quality, this can be separated into two large-scale processes. The first is the transport of air from one continent to another. The second is the downward transport of O_3 from the stratosphere to the Earth's surface, which is a key process that determines the baseline concentration of O_3, that is, the concentration of O_3 for a location without local or regional anthropogenic inputs. Climate-driven changes in environmental conditions (e.g., temperature, humidity, precipitation) affect both the production and removal of pollutants, including O_3 and PM, and must therefore also be considered.

2.1 Stratospheric-tropospheric exchange

The exchange of air between the stratosphere and troposphere can change tropospheric concentrations of O_3. In a relatively clean atmosphere, this effect may be quantifiable. Ozonesonde profiles of the concentration of O_3 have been collected since 1987 in New Zealand. These have been used to evaluate atmospheric models. Using these models, it has then been estimated that, between 1960 and 2010, there has been a decrease in concentration of 4 μg O_3 m^{-3} in the lowest 1.5 km of the atmosphere (near the ground) that was attributed to stratospheric O_3. That is, this decrease in concentration of O_3 at ground level is the combined effect of decreases in stratospheric O_3 due to ozone depleting substances (ODS) and changes in transport from the stratosphere.[194] Such an attribution is very difficult from ground-based measurements in the Northern Hemisphere (e.g., ref.[7]) because of the large variations in

sources. However, more accurate estimates are possible using ozonesondes measuring at 5 km above the surface and at high altitude sites well away from local pollution sources and hence also much closer to the stratospheric source as well.[64] From an analysis of measurements made at the Jungfraujoch in Switzerland (3.6 km altitude, 1988–2008) and a chemical transport computer model, it is estimated that 30% of the O_3 is attributable to stratospheric sources, and 95% of the variation at a monthly timescale is attributed to variations in stratospheric input. Trends in the measurements for the 20-year period are variable and not well captured by the computer simulation.[64] A study of measurements over the USA found evidence that enhanced ground-level O_3 followed specific meteorological conditions indicating enhanced transport of stratospheric air to the surface.[106] Model calculations suggest that significant changes (+ 50%) in stratospheric-tropospheric O_3 exchange could occur by 2100, as a result of changes in both climate and ODS.[127]

2.2 Effects of climate change on air quality

Air quality is directly affected by several environmental conditions including temperature, humidity, clouds and precipitation, local wind speed and long-range transport by winds, as well as land and vegetation type (e.g., urban vs forested settings). Many of these conditions are sensitive to both climate change and stratospheric O_3 depletion. For example, stratospheric O_3 depletion has already caused large changes in the weather of the Southern Hemisphere,[151] with probable (but as yet unquantified) effects on urban and regional air quality.

Increasing global temperatures are expected to lead to poorer air quality. Current observations point to a co-occurrence of elevated temperatures, high O_3, and high $PM_{2.5}$ at ground level in the eastern USA, suggesting a direct link between elevated temperatures and poorer air quality.[157] Similarly, in China, it has been estimated that the severe haze events with significant health impacts are correlated with lower wind speeds, driven by climate change.[99]

Modelling the impact of future climate change on air quality is difficult. Firstly, there is a need to consider the various drivers of change, such as changes in greenhouse gas concentrations and, for the southern hemisphere, recovery from the spring-time depletion of stratospheric O_3 (see Chapter 1). Then, for reliable estimates of impacts, it is necessary for the model to capture changes in wind speed and direction, temperature, rainfall, and cloudiness. Estimates of the impacts are known to be affected by things like the assumed building heights within the urban environment.[71] Ideally, estimates of likelihood of wildfires also need to be included.[84]

Recent estimates have been made for India for the period up to 2050, suggesting increases in surface O_3 in the north due to climate change.[90, 144, 151] These changes are attributed to changes in sources and sinks of O_3. For India, concentrations of $PM_{2.5}$ are predicted to increase at all latitudes due to climate change,[144] although the predicted changes depend on changes in human activity.[90] For Europe, an ensemble of models predict, for 2050, decreases in concentrations of surface O_3 in summer and increases in winter, with the magnitude (and significance of the trends) dependent upon the magnitude of the changes in emissions.[181] Similar general trends were predicted for deaths from O_3 in the USA.[6]

3 Effects of UV radiation on air quality

UV radiation drives photochemical reactions that transform emitted chemicals, such as hydrocarbons and nitrogen oxides, into more toxic secondary pollutants such as O_3 and particulate matter (PM). While emissions are obviously of primary importance, the rate of formation of secondary pollutants is limited by the availability of UV photons (see **Fig. 3**). UV radiation also regulates the self-cleaning ability of the troposphere by forming highly reactive hydroxyl radicals (OH) that react with many pollutants and accelerate their removal from the atmosphere.

3.1 UV radiation and ozone at the Earth's surface

Ozone has long been recognized as a significant concern in both urban and rural environments. A major review of the observations and trends has been undertaken.[25, 49, 53, 95, 129, 158, 191] We highlight some of the results of these assessments, as well as the relevance of stratospheric O_3 changes to ground level ozone.

The assessment of the importance of any changes in O_3 at ground level depends on who (or what) is exposed. A range of metrics have been developed and adopted in various regions. For short-term human exposure, one metric used is the 4^{th} highest daily maximum 8-hour running mean (4MDA8). For plants, a cumulative measure of O_3 exposure is generally accepted as being more appropriate, with an "accumulated exposure over a 40 ppbv (80 μg m^{-3}) threshold" (= AOT40) is often used, typically calculated from hourly averages for the growing season.[166]

Concentrations of O_3 at ground level have changed significantly in recent years, with the direction and extent of the change being dependent on location, broad regions showing decreases and increases, as shown in **Fig. 4**.[49] These changes are primarily a response to changes in emissions of precursors to O_3 (primarily changes in NO_x and volatile organic compounds). There have been increases in emissions where there has been rapid economic growth and decreases with the implementation of emission controls.

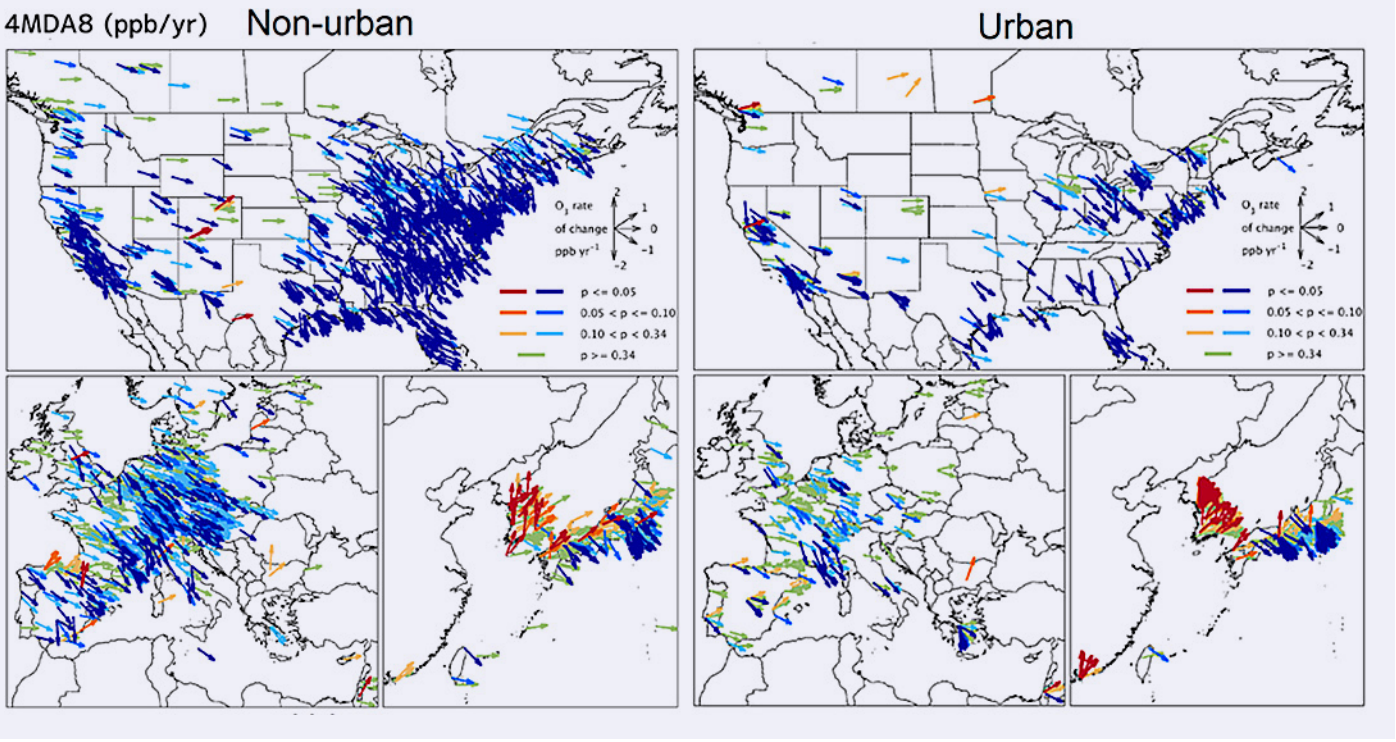

Fig. 4 **Trends in concentration of O_3 at ground level for the 15-year period (2000–2014), measuring O_3 with the human health related metric 4MDA8. The top panels on both sides are for North America, the lower left is for Europe and the lower right side is East Asia. Blue arrows indicate a decrease in concentration of O_3 and red an increase. The dark colours (red/blue) indicate a trend that is significant at the 95% confidence level. Lighter shades indicate lower levels of significance (from ref.[49]).**

The distribution of concentrations of O_3 by site is also changing as emissions (and emission controls) change. As an example, **Fig. 5** shows the changes in concentrations of surface O_3 observed in Berlin, a pattern of change seen in many locations where the yearly average concentration of surface O_3 is decreasing. There is a clear decrease in events with high concentrations of O_3 and an increase in the number of periods with more moderate concentrations. There is also a decrease in the number of periods of low concentrations of O_3 (< 20 μg m^{-3}). These periods of low concentrations of O_3 were caused by the reaction of O_3 with NO_x, and there has been a reduction in the concentration of NO_x in these urban atmospheres. In regions where increases in precursor emissions dominate, the opposite pattern (increased frequency of periods with low and high concentrations of O_3) is observed.

The ability of computer models to replicate observed concentrations of surface O_3 has been limited, with models predicting lower concentrations of O_3 in winter than observed and higher concentrations in summer (by up to 20 μg m^{-3}), particularly in N America.[74] The model biases in winter are believed to be due to not including the impact of long-range transport of air.[107, 118] A recent modelling study suggests that 66% of the higher concentrations in summer could be due to models not adequately describing the impact of the forest canopy on reducing solar radiation and modifying movement of air.[118] This suggests that forecasts of concentrations of O_3 at ground level could soon become more robust.

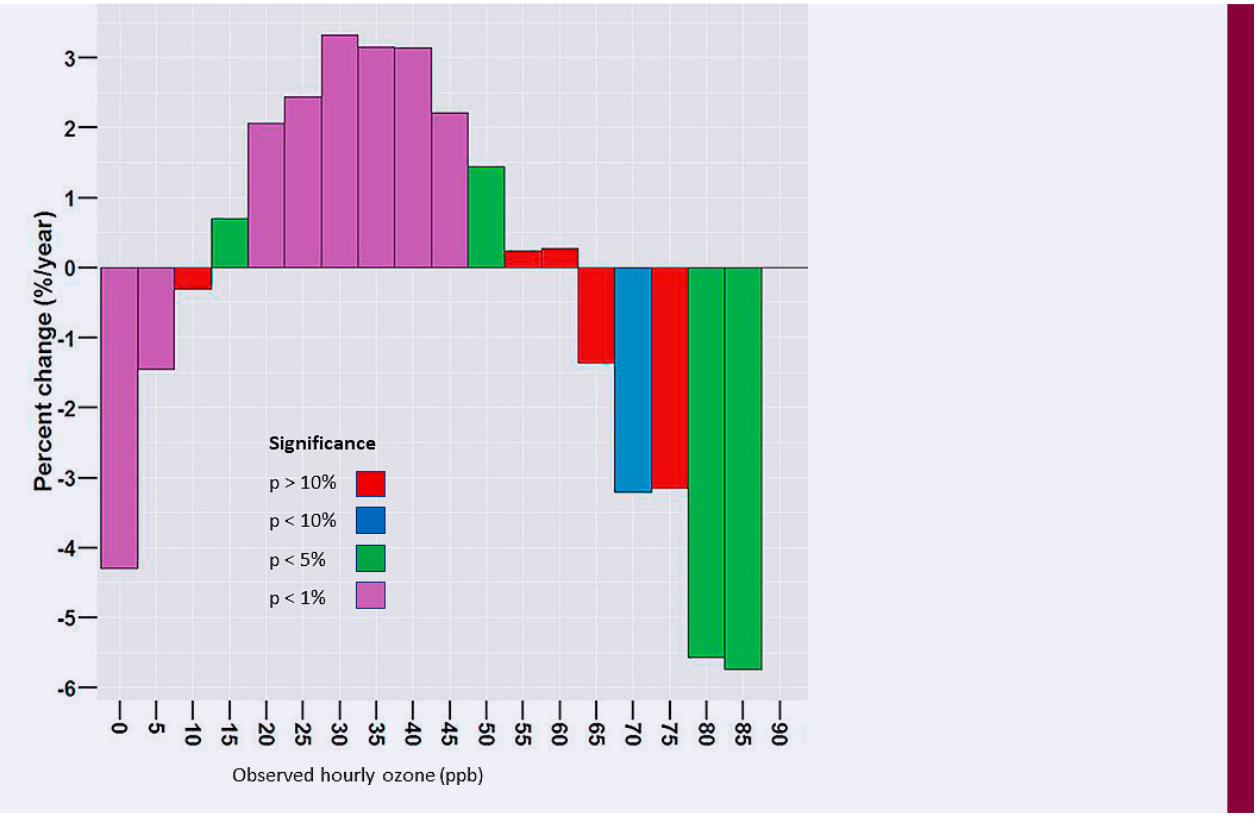

Fig. 5 **Changes in observed hourly average ozone concentration at ground level for Berlin for the period 1990 to 2013. Observations have been sorted into 5 ppb wide "bins". Plotted is the trend in the number of observations within each bin. The colour indicates the probability (p) that the change is not significant (from ref.[94]).**

3.1.1 Future changes in surface ozone

Future concentrations of O_3 at ground level will depend on a range of environmental factors and the relative importance of these factors will depend on location. Estimates indicate that, due to climate change, there will be an increase in O_3 in the lower atmosphere at most latitudes, with the largest changes being due to an increase in the concentrations of NO_x driven by an increased frequency of lightning in the tropics.[13,14] The absolute magnitude of these changes in surface O_3 will depend on the increases in the concentrations of greenhouse gases. In addition to this, an increase in tropospheric O_3 of similar magnitude is expected due to downward transport of stratospheric air (see section 2.1) that will be altered by the recovery of stratospheric O_3 through the phase-out of ODS[14] and the response of stratospheric O_3 to climate change.[21] In northern mid-latitudes, these changes will be largely offset by a reduction in surface O_3 due to a reduction in precursors of O_3 from the control of emissions implemented in many countries. However, for the tropics, the background O_3 concentration is expected to increase by around 10% by 2050. These global scale changes help define the underlying concentration of O_3 that is experienced in urban and regional areas. More local sources (and sinks) of O_3 then determine the concentrations that humans and plants are exposed to.

3.1.2 Modulation of tropospheric ozone by changes in UV radiation

If, as expected with the ongoing success of the Montreal Protocol, amounts of O_3 increase in the stratosphere, reactions in the troposphere dependent upon UV radiation will slow down, thereby decreasing both the production and destruction of surface O_3 (see also **Fig. 3**).[68] Coarse resolution spatial modeling (4° x 5°, roughly 400 x 400 km at mid-latitudes) predicted this will cause an increase in surface O_3 over the USA.[196] However, it is expected that there will be areas within cities where the slower production should reduce concentrations of O_3.[9] Running a model of atmospheric chemistry at higher spatial resolution (12 km x 12 km) over the contiguous USA,[68] highlights that the impact of increases in stratospheric O_3 on ground level O_3 is not uniform, with decreases in the concentration of O_3 at locations in or near major cities, and increases elsewhere (**Fig. 6**), with a population-weighted increase in concentrations of O_3 overall. The increase outside cities is small (about 1 μg m^{-3}) but represents an additional negative effect on air quality. Effects on human health will depend on the balance between the direct impact of decreased UV radiation on health (see Chapter 2) and reduced air quality, both impacts which involve significant uncertainties.[43]

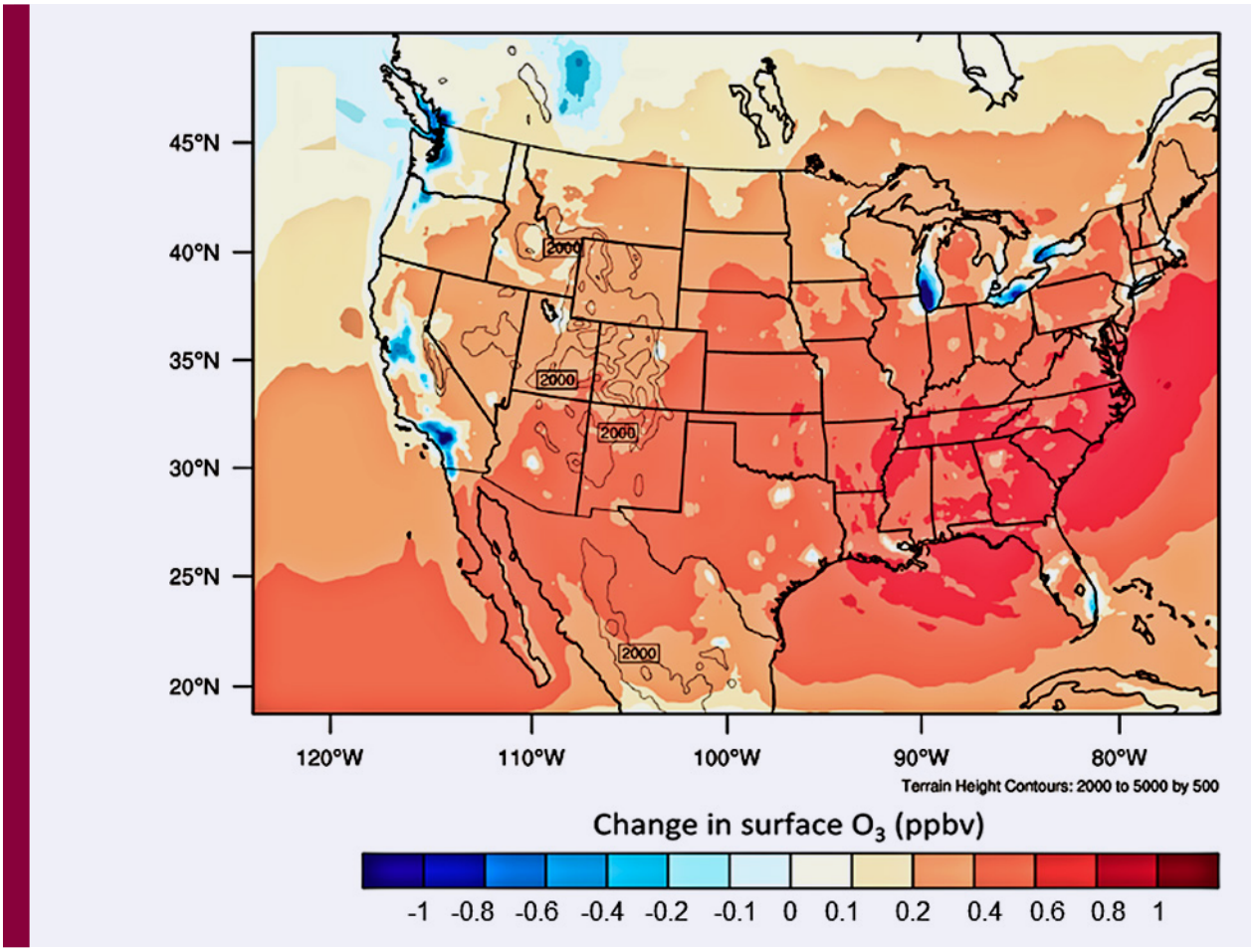

Fig. 6 **Changes in ground-level O_3 because of a change from current (2000–2010) stratospheric ozone to that predicted for 2085, calculated for a 12 x 12 km grid (from ref.[68]).**

3.2 Particulates and UV radiation

Particulate matter (PM) suspended in the atmosphere is a major component of air pollution. Also known by other names such as aerosols, haze, and smog (**Fig. 7A**), elevated concentrations of PM have been associated with adverse effects on human health (see below), degradation of visibility (as they scatter light), modification of the hydrological cycle (through interactions with clouds and precipitation (e.g., ref.[182])), and reduction in efficiency of photovoltaic solar collectors.[103] Particles are generally complex mixtures of different components (see **Fig. 7B**) that include both primary (e.g. soot) and secondary (e.g. sulfates and organics) compounds. A substantial fraction of PM is influenced by the chemical and physical state of the atmosphere and is therefore sensitive to changes in environmental variables including UV radiation, temperature, winds, and humidity.

Fig. 7 **(A) Photochemical haze over Mexico City seen from approaching aircraft. (B) Electron microscopy image of a typical particle collected from the photochemical haze (from ref.[1]).**

It is useful to distinguish between PM emitted directly from sources at the Earth's surface (primary aerosols), and those formed in the atmosphere by condensation of various gases (secondary aerosols). These secondary aerosols include sulfate, nitrate, and a multitude of organic compounds that condense following atmospheric reactions of emitted precursor gases such as SO_2, NO, and hydrocarbons.[159] Primary aerosols include dust/soils, sea salt, biological particles (e.g., pollen) and soot, and other carbonaceous particles produced during combustion of fossil fuels and wildfires. Natural and anthropogenic sources contribute to both primary and secondary aerosols, e.g., organic aerosols may be formed from emissions of isoprene and terpenoid compounds from plants, as well as from fugitive emissions from industrial and transportation sectors.

UV radiation has a direct role in the formation of secondary aerosols by producing hydroxyl (OH) radicals that oxidize (harmful) precursors to chemicals that will more readily condense into particles, e.g., SO_2 to H_2SO_4 or NO to HNO_3. Increases in UV radiation lead to more rapid formation of secondary PM, resulting in more intense local smog episodes. Changes in weather patterns (and hence climate) can affect both primary and secondary aerosols, e.g., by changes in wind-driven transport patterns, by temperature effects on condensation and/or evaporation, uptake of water (deliquescence/efflorescence) on particles, and eventual removal by incorporation into precipitation.

3.2.1 Distribution and trends of aerosols

Measurements of aerosols are made routinely in many cities and regions as part of observational networks monitoring air quality, using a variety of analysis techniques (e.g. refs[104, 124, 165, 197]). In recent years, estimates of the distribution of aerosols over large geographical scales have become available from satellite-based instruments.[93, 150, 184] In addition to providing a global climatology of aerosols,[150] this has allowed more detailed assessment of aerosols in specific regions that had previously only sparse measurements, e.g., over China,[190] the Mediterranean Sea,[55] India,[81] and the Saharan desert.[116] Combined with ground-based measurements and numerical models, these observations clearly show the contribution to PM from sulfate emitted by urban and industrial activities, black and organic carbon mostly from biomass burning, and wind-driven dust and sea-salt (see **Fig. 8**).

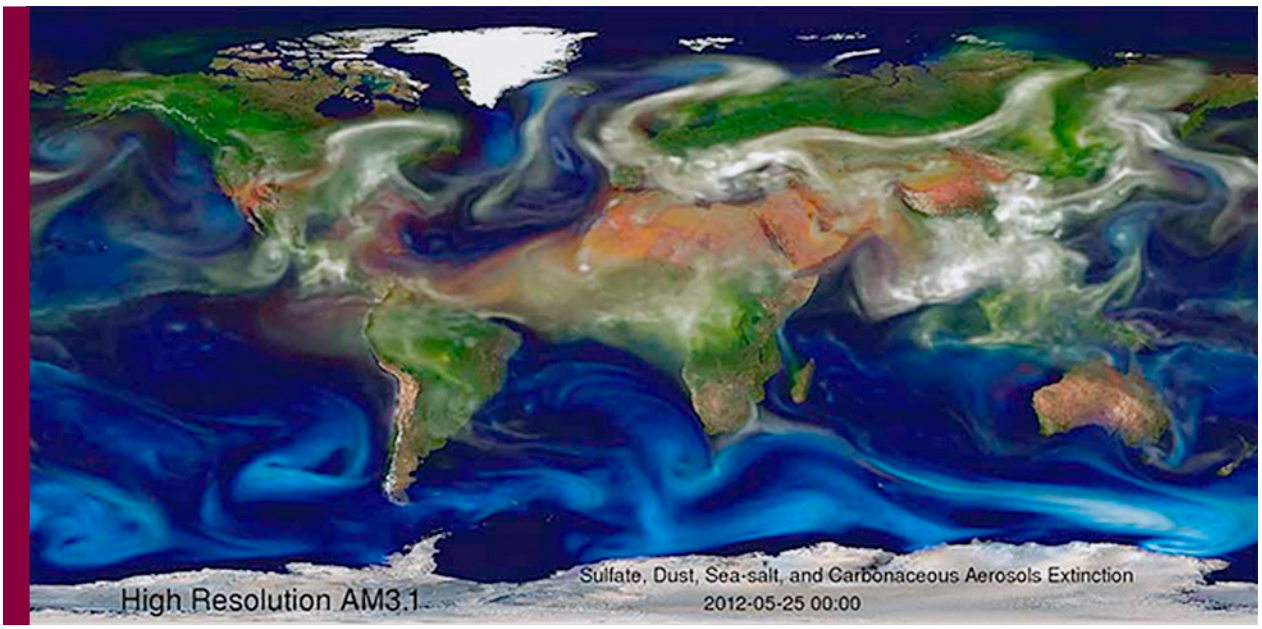

Fig. 8 **Aerosol plumes colored according to predominant particle type: dust (orange-red), sulfate (white), black carbon and organics (green), and sea salt (blue), for one day in 2012 (from Paul Ginoux, https://www.gfdl.noaa.gov/visualizations-aerosols-and-clouds)**

Long-term trends in aerosols depend strongly on geographic location and reflect several regional factors, such as economic development and emission controls for aerosols and their precursors. This geographic dependence is illustrated in **Fig. 9** for the period 1990–2015. Strong positive trends are seen over China and the Indian subcontinent (see also ref.[167]), with rates of increase reaching 3% per year (change in optical depth of 0.3 in 25 years), while negative trends of similar magnitude are seen over central Europe and the Eastern USA.[22, 130] The changes in PM over Europe have been calculated to have increased surface O_3 through enhanced photolysis and increased biogenic volatile organic compound (BVOC) emissions.[138] The trends observed are also reflected in changes in aerosol properties, as the dominant source of the particles changes.[201] These trends in aerosol loading and composition have important implications for health effects as discussed below.

In calculating conditions within extreme aerosol pollution events, Li *et al.*[100] found significant changes in UV intensity at ground level that altered the chemical composition and hence air quality. Validation of the models with observations in cases like this should lead to higher confidence in estimates of changes in air quality due to changes in UV radiation, and hence the impact of ozone recovery on air quality.

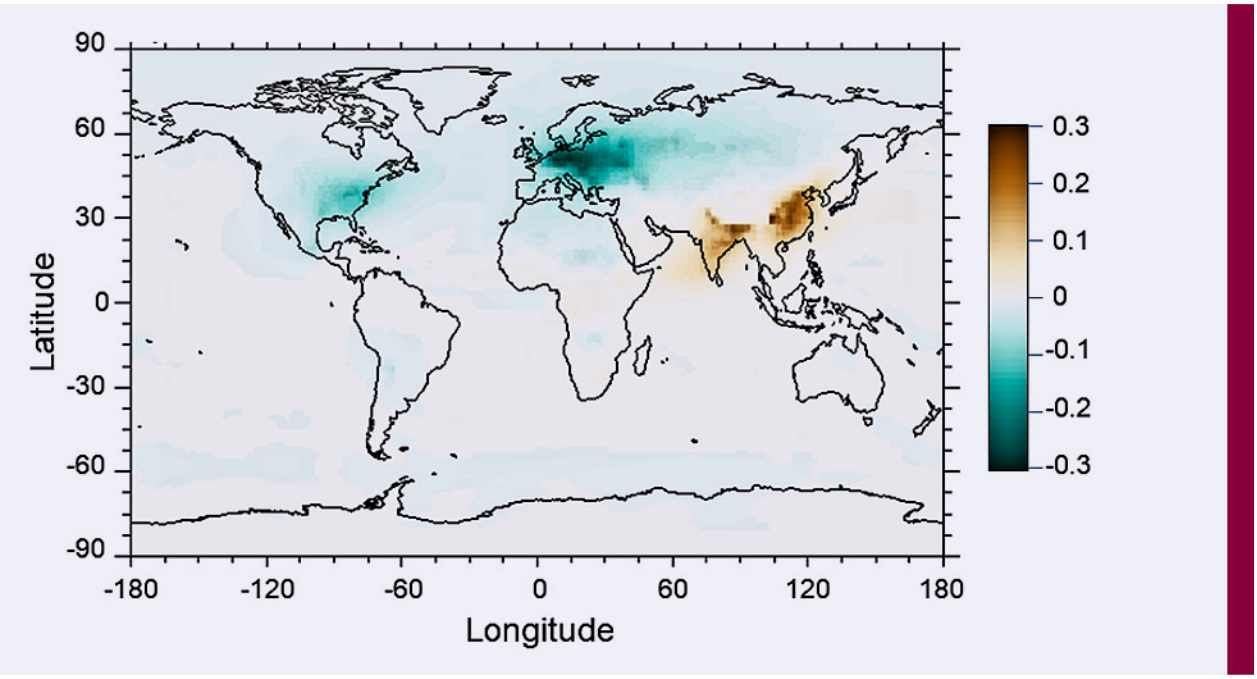

Fig. 9 **Changes (1990 to 2015) in the aerosol column optical depth at 550 nm, computed as the mean of six global models (from ref.[130]).**

3.3 UV radiation and the atmospheric global oxidation capacity

As noted before, the hydroxyl radical is a highly reactive molecule that initiates the chemical transformation of many gases in the atmosphere (e.g., volatile organic compounds). This transformation typically accelerates the removal of these gases from the atmosphere, although some of the short-lived intermediate products formed can also be harmful (e.g. secondary aerosol). Hydroxyl radicals may be formed in several ways in the atmosphere, but the main route is via the photolysis of O_3 by UV radiation with a wavelength less than 330 nm (**Fig. 3**).

The concentrations of OH are highly variable in both space and time because of these production- and destruction-reactions. At the same time, however, a change in the global average concentration of OH can have a significant impact upon the removal of many important air pollutants, as well as some greenhouse gases (e.g., methane) and ozone-depleting substances (e.g., HCFCs).

Because of the importance of OH for the chemistry of the atmosphere and in particular for air quality, there have been several approaches used to assess changes in the global concentrations of tropospheric OH. The most widely used has involved the assessment

of trends in the concentration of methyl chloroform (1,1,1-trichloroethane), which is a synthetically produced compound that has been regulated under the Montreal Protocol. Methyl chloroform is primarily removed from the atmosphere through reaction with OH. Given a reasonable estimate of the amount of methyl chloroform released and a well-known atmospheric concentration, the removal rate (and hence the concentration of OH) can be inferred (e.g., ref.[148]). One limitation of this method is that the concentration of methyl chloroform is rapidly decreasing due to the implementation of the Montreal Protocol and soon concentrations will be too low to be useful for estimating concentrations of OH.[105]

Estimates have also been derived from the observed concentrations of methane, which is also primarily removed from the atmosphere by OH. However, this method is hindered by a lack of knowledge of the magnitude and variability of sources of methane.[12] A recent summary of the difficulties in quantifying the methane budget and therefore global concentrations of OH recognizes the critical need for more work in this area.[147] An alternative method has been proposed that uses four halocarbon compounds to estimate the global concentrations of OH (HFC-32 (CH_2F_2), HFC-134a (CH_2FCF_3), HFC-152a (CH_3CHF_2), and HCFC-22 ($CHClF_2$)).[105] In their initial assessment, the authors found that the combination currently did as well as methyl chloroform alone and may provide a useful method in the years to come as the concentration of methyl chloroform continues to decrease.

Model estimates of trends in concentration of OH are problematic due to uncertainty in the chemical reactions that produce OH and the sources and emissions of precursors. There also remain significant uncertainties in the rates of key chemical and photochemical reactions.[131, 133] This is evidenced by the difficulty models have in predicting the correct ratio of OH between the hemispheres.[142] A recent study of the atmosphere over the tropical West Pacific found that estimates of concentrations of OH in the troposphere could be changed by 20–30% (in both directions) by correcting the concentrations calculated for key precursors to those observed in the field.[132] A recent model of global OH suggests that the generation of OH from the oxidation of biogenic volatile organic compounds (BVOCs) has been underestimated.[97] This would make the concentration of OH in the atmosphere much less dependent upon anthropogenic emissions, and significantly alter the predictions of future atmospheric composition. These emissions of BVOCs also may be stimulated by exposure to UV-B radiation (see Chapter 3 and ref.[110]). Future emissions of BVOCs will be altered by changes in land-use and climate change (see Chapter 3 and ref.[60])

4 Impacts of air pollution on human and environmental health

Exposure to air pollution is known to be detrimental to the health of humans as well as natural and cultivated ecosystems. The direct effects of exposure to UV radiation on human health and plants (including terrestrial organisms and crops) are discussed in Chapters 2 and 3, respectively. Here, we focus on how two principal pollutants, surface O_3 and PM, whose UV-dependent formation was discussed above, are considered to affect human health and agricultural yields. For human impacts, we note the existence of both large-scale assessments, carried out either by government agencies or others (NGOs), as well as a large growing body of scientific literature based on analyses ranging from molecular to clinical and epidemiological scales.

4.1 Adverse effects of poor air quality on human health

4.1.1 Global and regional assessments

The impact of PM on human health is now widely acknowledged, although quantitative estimates vary considerably among studies. **Table 1** summarizes premature mortality derived by numerous large-scale studies. Global estimates range by a factor of three, from 1.4 to 4.2 million deaths per year.

Table 1 **Estimates of global and regional mortality for particulate matter and ozone, million per year.**

Source	Year	Mortality per year (millions)		Region
		Particulate matter	Ozone	
OECD[137]	2010	1.4	0.35	Global
	2050	3.6	0.75	Global
Fang *et al.* 2015[45]	2000	1.5	0.38	Global
Lelieveld *et al.* 2015[96]	2010	3.2	0.14	Global
GBD 2016[56]	2005	3.7	0.19	Global
	2016	4.1	0.23	Global
Malley *et al.* 2017[119]	2010		1.04–1.23	Global
Fann *et al.* 2012[46]	2005	0.05–0.2	0.005	USA
GBD 2016[56]	2016	1.1	0.07	China
	2016	1.0	0.09	India
	2016	0.15	0.011	Western Europe
	2016	0.09	0.012	USA
EEA 2017[44]	2014	0.43	0.09	Europe
Malley *et al.* 2017[119]	2010		0.27–0.33	China
			0.40–0.45	India
			0.03–0.05	N. America

The geographic distribution of these deaths is presumed to follow closely the amount of $PM_{2.5}$, which is likely to penetrate more deeply into the respiratory system than larger particles. Changes in concentrations of $PM_{2.5}$ in the atmosphere since 1960 have been estimated and used to compute corresponding changes in aerosol-associated mortality (**Fig. 10**).[22]

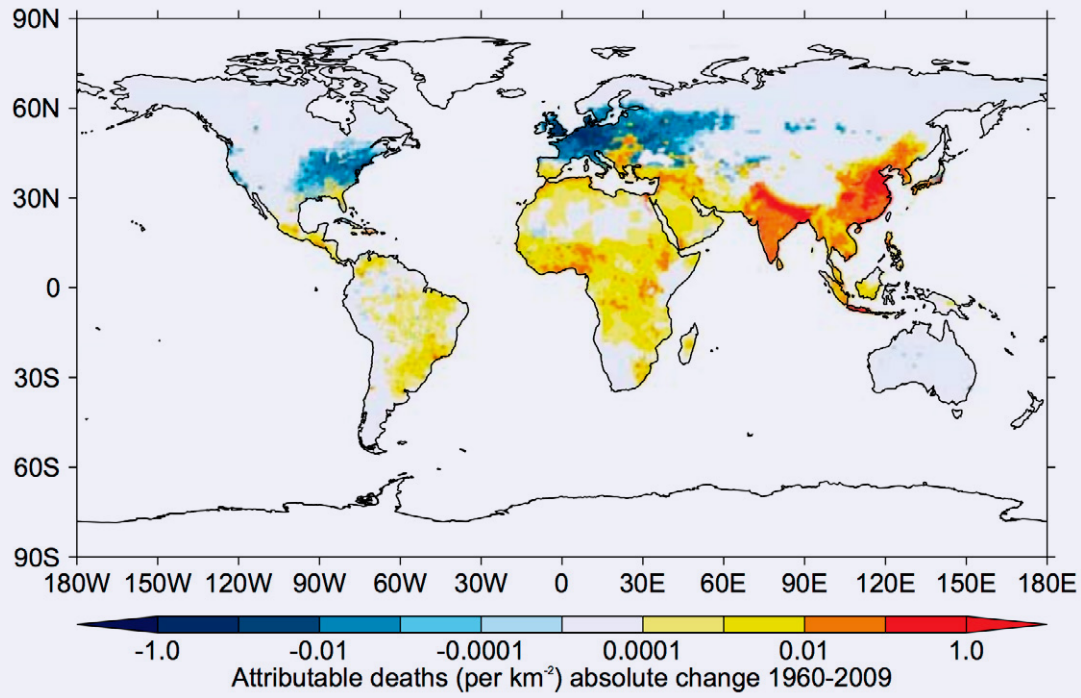

Fig. 10 **Changes in deaths globally due to particulates for the period 1960 to 2009 (from ref.[22]).**

4.1.2 Overview of recent human health studies

Reports of associations between poor air quality and various diseases in humans continue to accumulate in the literature. A large proportion of the global population is potentially exposed to excessive concentrations of atmospheric particulates.[160] For $PM_{2.5}$, it has been reported that, in 2016, 95% of the world's population was living in areas where ambient concentrations of $PM_{2.5}$ were greater than the World Health Organization annual average guideline (10 μg m^{-3}).[160] Global population-weighted concentrations of $PM_{2.5}$ were greater in 2016 (51.1 μg m^{-3}) than 2010 (43.2 μg m^{-3}), a change driven by increases in South-Asian countries. As was pointed out earlier,[12] outdoor air pollution is recognized as a Group-1 human carcinogen by the International Agency for Research on Cancer.[72] Many of the recent studies on the impact of air pollutants report an increased risk of many adverse (non-cancer) health effects with increased levels of air pollution.

Almost all epidemiological studies only report associations or linkages between a disease and exposures to one or more chemicals. It is important to understand that association or linkage is not proof that the exposure caused the disease (causality). As shown in the Hill guidelines of causality,[66] other information which supports the association must be considered.

Below, we provide an overview of recent studies on the adverse effects in humans that have been associated with air pollution. This is not a meta-analysis or systematic review, but is

provided to highlight the importance of air pollution to health, especially in countries and locations where air pollutants are found in large concentrations.[128] Because this section is based in the epidemiological literature, terms specific to this branch of science are explained in footnotes at first mention (as well as in the abbreviations). Many of these studies assessed exposures to air pollutants that included significant concentrations of gases and particulates of varying chemical composition. Therefore, it may not be possible to defensibly assign causality to a pollutant or sub-component of a pollutant, i.e., PM.

Effects of air pollutants on mortality. Several studies have assessed increased mortality arising from exposure to individual air pollutants in humans. A global estimate of deaths in persons ≥ 30 years of age attributable to O_3 was based on the results of exposure and respiratory mortality from the American Cancer Society Cancer Prevention Study II.[119] Mathematical models were used to estimate 6-month average exposures and risk thresholds corresponding to the minimum or 5th centile of O_3 exposures for 2010. The authors estimated that, globally, 1.04–1.23 million respiratory deaths in adults in 2010 were attributable to exposure to O_3. The study also indicated that increases in estimated attributable mortality were larger in northern India, southeast China, and Pakistan than in Europe, eastern USA, and northeast China. These results were consistent with an earlier regional study in the USA that reported a relative risk of death from respiratory causes of 1.040 (95% CI[16] 1.010, 1.067) is associated with an increment in concentration of O_3 of 20 μg m^{-3}.[79] A prospective study[17] of cancers other than lung cancers was carried out as part of the above Cancer Prevention Study II,[174] reported increased exposure to $PM_{2.5}$ (per 4.4 μg m^{-3}) was significantly positively associated with deaths from cancers of the kidney (HR = 1.14; 95% CI of 1.03, 1.27) and bladder (HR = 1.13; 95% CI of 1.03, 1.23). Increased exposures to NO_2 (increment of 12 μg m^{-3}) was positively associated with mortality from colorectal cancer (HR of 1.06; 95% CI of 1.02, 1.10). No association between any type of cancer was associated with O_3.

A study on the effects of increased concentrations of O_3 and total daily mortality was conducted in seven cities in Jiangsu Province, China (2013–2014).[27] Daily total mortality was 0.55% higher (Bayesian 95% credibility interval = 0.34–0.76) for each 10 μg m^{-3} increment in the 8-h average concentration of O_3, with a 2-day lag. Similar associations with exposure to ambient concentrations of O_3 were reported in Italy[136] and Iran.[86] A nationwide study in 272 Chinese cities between 2013 and 2015 showed that a 0.24% increase in daily mortality from all nonaccidental causes (95% Prediction Interval (PI[18]) = 0.13%–0.35%) was associated with an increment in 8-h maximum concentration of O_3 of 10 μg m^{-3}, approximately half that reported above.[189] However, no association between increased concentrations of O_3 and daily mortality from respiratory diseases was reported.

Exposure to particulates have also been associated with premature mortality. Exposures were modelled from measured values using geocoding, a national-level hybrid land-use regression and Bayesian maximum entropy interpolation. Based on 623,048 participants followed from 1982–2004 and 43,320 non-lung cancer deaths, higher exposures to $PM_{2.5}$ (per 4.4 μg m^{-3}) were significantly associated with increased risk of death from cancers of the kidney (Hazard Ratio[19] [HR] = 1.14; 95% CI of 1.03, 1.27) and bladder (HR = 1.13; 95% CI of

16 A confidence interval is an interval that will contain a population parameter a specified proportion of the time, 95% in this case.

17 A prospective study is an epidemiological study which follows disease incidence in a cohort over time.

18 Prediction Interval [PI] is a range of values in which future observations will fall, with a certain probability, given what has already been observed.

19 HR, the hazard ratio is the ratio between the responses observed in the exposed and control groups.

1.03, 1.23). Higher exposures to NO_2 (increment of 12 μg m^{-3}) were positively associated with mortality from colorectal cancer (HR of 1.06; 95% CI of 1.02, 1.10). No association between any type of cancer was associated with greater exposure to O_3. In a prospective cohort study of 189,793 older men (age > 40 in 1990 and 1991) in 45 locations in China, non-accidental mortality from several causes was associated with concentrations of $PM_{2.5}$.[188] Annual average levels of $PM_{2.5}$ were estimated from measurements and models and, for the period of investigation (2000–2005), ranged from 4.2 to 83.8 μg m^{-3}. HRs and the (95% CIs) for a 10-μg m^{-3} increment in $PM_{2.5}$ were 1.09 (1.08–1.09) for non-accidental causes; 1.09 (1.08–1.10) for cardiovascular disease; 1.12 (1.10–1.13) for chronic obstructive pulmonary disease (COPD); and 1.12 (1.07–1.14) for lung cancer. The analytical model included adjustments for smoking and other lifestyle variables. These data provide consistent evidence of increases in mortality associated with exposures to air pollutants.

Effects of air pollution on the respiratory system. The respiratory system is expected to be the primary target of air pollutants. This is the primary site of uptake and where concentrations and effects would be greatest. This has been shown in several studies[12] with the suggested mechanisms involving inflammation, vasoconstriction, and coagulation of blood.[28] Some studies reported on mortality only (included above), while others also reported on ill health (morbidity), which is discussed below.

A meta-analysis of the relationship between ambient outdoor air pollution and exacerbation of chronic obstructive pulmonary disease (COPD) was based on 37 papers.[40] In this analysis of a total of 1,115,000 COPD-related acute events and 130,000 deaths, the authors indicated that there was a significant positive association between concentrations of pollutants ($PM_{2.5}$, NO_2, and SO_2) and COPD-related morbidity and mortality. Unfortunately, exposure to O_3 was not included in the study. A study of lung function in response to daily measures of air pollutants was carried out in Belgium.[75] Several repeated measures of lung function were obtained from 2449 adults over a 4-year period between 2011 and 2015. No significant association was observed for O_3, but several measures of lung function decreased in response to elevated concentrations of PM_{10} and NO_2 in the days prior to testing.

Effects of air pollution on human health are a global issue and linkages like the above have been reported from several countries.[85, 91, 102, 108, 141] Mortality from acute respiratory distress syndrome (ARDS) was associated with exposure to O_3 and particulate matter.[152] After controlling for other (unstated) variables in the model, treatment in a hospital located in an area with high O_3 was associated with an increased odds ratio (OR[20]) of mortality of 1.11 (95% CI; 1.08–1.15, $p < 0.01$) for in-hospital mortality. Adjusting for all factors, for each 20-μg m^{-3} increment in the concentration of O_3, the OR for mortality was 1.07 (95% CI; 1.06–1.08, $p < 0.01$). Exposure to O_3 is associated with changes in lung function in asthmatics as well as in the general population.[82, 154] A 20-μg m^{-3} increment in the concentration of O_3 was associated with increased incidence of cough and stuffy nose (OR; 1.23, 95% CI: 1.00, 1.51), as well as absenteeism in school children in Greece.[154] In another study on childhood lower respiratory diseases in China,[205] an interquartile range increment in concentrations of PM_{10} (72 μg m^{-3}), NO_2 (26 μg m^{-3}), and SO_2 (16 μg m^{-3}) significantly increased the daily childhood lower respiratory diseases with 6-days cumulative effect (difference of estimates was 2.8%, 95% CI: 0.6–5.0%; 4.1%, 1.2–7.0%; 5.6%, 2.6–8.6%, respectively). Childhood lower respiratory diseases were not significantly associated with interquartile increments in concentration of $PM_{2.5}$ (42 μg m^{-3}), O_3 (76 μg m^{-3}), and CO (410 μg m^{-3}).

20 Odds ratio [OR] Odds that an outcome will occur given a particular exposure, compared to the odds of the outcome occurring in the absence of that exposure.

Effects on the cardiovascular system. The cardiovascular system is probably the second most sensitive system to air pollutants in humans. Many studies have reported associations between estimated exposure to air pollutants and cardiovascular mortality and morbidity in adults and children.

As part of the Black Women's Health Study in the USA, incidence of hypertension was investigated in participants representing 348,154 person-years from 1995 to 2011 with 9,570 cases identified.[34] Exposures were estimated using a spatiotemporal model from the US EPA and were based on measured values from ground-level monitoring sites and satellite observations. Several covariates, such as self-reported weight, smoking and alcohol history, and hours/week of vigorous exercise were considered. Daily 8-hour maximum concentrations of O_3 were averaged for the years 2007–2008 to approximate the long-term average exposure. Long-term exposure to greater concentrations of O_3 (the highest quintile[21] of exposure concentrations, 82–112 μg m^{-3}) was associated with increased incidence of hypertension (HR = 1.09, 95% CI; 1.00–1.18) but the opposite was reported for NO_2 (48–73 μg m^{-3}) where higher NO_2 concentrations were related to lower incidence (HR = 0.92, 95% CI; 0.86–0.98). In a 272-city study in China for data from 2013–2015,[189] a positive association between 10 μg m^{-3} increments in concentration of O_3 and higher daily mortality was reported from cardiovascular diseases (0.27%, 95%, PI = 0.10–0.44%), including hypertension (0.60%. 95% PI = 0.08–1.11%), coronary diseases (0.24%, 95%, PI = 0.02–0.46%), and stroke (0.29%, 95% PI = 0.07–0.50%). While the proportional increases were small, the effects in large populations were significant.

Particulates have also been associated with effects on the cardiovascular system. A large study on Medicare patients was conducted in the USA.[41] The study included data on 60,925,443 individuals with 460,310,521 person-years of follow-up from 2000 through 2012. Exposures were based on postal code, and 10-μg m^{-3} increments in annually averaged concentration of $PM_{2.5}$ were associated with an increase in all-cause mortality of 7.3% (95% CI, 7.1–7.5). A statistically significant increase in mortality was also observed for a 20-μg m^{-3} increment in O_3 concentration. Deaths among men, blacks, and people with Medicaid eligibility were more than that in the rest of the population. The authors point out that there was evidence of adverse effects related to exposures at O_3 concentrations below the current air quality criterion in the USA (140 μg m^{-3}).

Several large studies have shown linkages between heart attack and stroke, and ambient concentrations of air pollutants. A study on relative risk of hospitalization for acute myocardial infarction in Wallonia (Belgium) between 2008 and 2011 showed a stronger association between heart attack and incremental concentrations of NO_2 (interquartile range[22] [IQR] = 14–26 μg m^{-3}, relative risk[23] [RR] = 1.029; 95%CI, 1.009–1.049, P = 0.005) than PM_{10} (IQR = 14–30 μg m^{-3}, RR = 1.012; 95%CI, 1.001–1.023, P = 0.027).[33] There was no significant association between risk of heart attack and incremental concentration of O_3 (IQR = 33–57 μg m^{-3}). A study in China with 13,535 patients with acute ischemic stroke hospitalized to 12 participating centers showed an association between cardioembolic stroke and PM_{10} and concentrations of SO_2.[31] Odds ratios were greatest for SO_2 (1.56, 95% CI 1.13–2.16). A multicity (14 large cities) case-crossover study of the association between ambient air pollution and hospitalization for ischemic and haemorrhagic stroke between 2014 and 2015 was carried in

21 Quintile, any of the four values that divide the items of a frequency distribution into five classes with each containing one fifth of the total population. The upper quintile of a data-set includes the values falling between 80 and 100% in cumulative frequency distribution.

22 The interquartile range [IRQ] is the difference between 75th and 25th centiles in a cumulative frequency distribution of values.

23 The relative risk [RR] is the risk of an outcome relative to that for an unexposed population.

China.[111] Based on 200,958 cases of ischemic stroke, an interquartile increment in the six-day average concentration of PM_{10} (86 μg m^{-3}), SO_2 (38 μg m^{-3}), NO_2 (26 μg m^{-3}), CO (810 μg m^{-3}), and O_3 (67 μg m^{-3}) was associated with a significant increase in admissions only for SO_2 (1.6%, 95% CI 1.0– 2.3%) and NO_2 (2.6%, 95% CI 1.8–3.5%). For hemorrhagic stroke, the only significant association was with concentration of NO_2 on day of admission. In a second paper[112] based on the same exposure data but testing the effects of air pollutants on hospitalization for acute myocardial infarction, the only significant increases found were associated with SO_2 (2.0%, 95% CI, 1.2–2.9%) and NO_2 (2.2%, 95% CI 1.4–3.1%). Significant increases in hospitalization were not observed for O_3. In another study in China on 147,624 stroke admissions in Beijing in 2013–2014 showed a slight increase (0.82% and 0.73% resp.) in admissions with every 10 μg m^{-3} same-day increment in concentration of NO_2 and SO_2.[70] Similar results were reported in a study in Taiwan on hospital admissions for myocardial infarction.[30] This increase was reported for warm (> 23°C) as well as cool days (< 23°C) and was statistically significant. In contrast, a study of 1758 incident reports of stroke in South London (UK) between 2005 and 2012 found no evidence of a significant association between all stroke or ischaemic stroke and same day increased exposure to $PM_{2.5}$ (IQR = 10.1–18.0 μg m^{-3}), PM_{10} (IQR = 17.2–28.9 μg m^{-3}), O_3 (IQR = 23.2–49.3 μg m^{-3}), NO_2 (IQR = 33.6–53.6 μg m^{-3}), or NOX (IQR = 50.5–92.4 μg m^{-3}).[20] The authors also reported negative (but not significant) associations between incidence of haemorrhagic stroke and an increment in concentration of 10 μg m^{-3} of PM_{10} (-14.6%, 95% CI 0.7–26.5%) and $PM_{2.5}$ (–17.0%, 95% CI, 3.3–33.3).

Kawasaki disease is an acute and multi-systemic vasculitis that occurs predominantly in infants and young children from East Asia and the Pacific. Kawasaki disease can cause myocardial infarction and sudden death in children and young adults. The seasonality of the disease has suggested an environmental cause, although there is also an increased genetic risk.[19] In a study of 695 hospital admissions for Kawasaki disease in Taiwan (2000–2010), an increased risk was associated with 58 μg m^{-3} increments in concentrations of O_3 on the day of hospitalization in the summer months only (OR adjusted for temperature, humidity, and wind = 1.21; 95% CI, 1.01, 1.44).[80] There were no associations with concentrations of CO, NO_2, PM_{10}, or SO_2. The authors noted that a biological mechanism for the putative effects of O_3 has not been elucidated. As has been pointed out,[89] additional studies from other regions are needed to confirm the association of Kawasaki disease with ground-level concentrations of O_3.

A meta-analysis of the association between air pollution and cardiac arrest outside a hospital showed significant associations with 10-μg m^{-3} increments of PM_{10}, $PM_{2.5}$, NO_2, and O_3.[204] The largest association was with $PM_{2.5}$ (3.9%; 95% CI, 1.2–6.6%).

In terms of morbidity, a study in Taiwanese adults between 2001 and 2014 reported a small but statistically significant association between $PM_{2.5}$ and blood pressure and risk of hypertension.[200] A total of 125,913 non-hypertensive participants was selected from a group of 361,560 adults ≥ 18 years-old for follow-up. Exposures to $PM_{2.5}$ were estimated from the participants address using a satellite-based spatio-temporal model. A 10-μg m^{-3} increment in the 2-year average concentration of $PM_{2.5}$ was associated with an increase in systolic blood pressure of 0.45 mm Hg (95% CI, 0.40–0.50). The same increment in exposure was associated with a 3% increase in risk of developing hypertension (95% CI, 1–5%). Similar results were reported in a study of 9,354 school children (5–17 years old) in China.[195] Increments in the 5-day mean interquartile concentrations of PM_{10} (50 μg m^{-3}) and O_3 (53 μg m^{-3}) were associated with elevations of 2.1 mm Hg (95% CI, 1.7–2.4) and 3.3 mm Hg (95% CI, 2.9–3.7) in systolic blood pressure, respectively. The ORs for an increment of 1 IQR ranged from 1.6 to 2.7

for PM_{10} and 1.12 to 3.33 for O_3 and were significant. In another study, an analysis of daily visits to emergency rooms in Beijing, China between Jan 1, 2014 and Dec 31, 2015 (7,088,309 visits) showed significant associations with same-day concentrations of O_3.[172] A 10-μg m^{-3} increment of 8-hour averaged O_3 was significantly associated with a 0.24% (95% CI, 0.21%–0.26%, $P < 0.01$) increase in daily visits to emergency rooms across the entire study period. When concentrations were ≤ 100 μg O_3 m^{-3}, an increment of 10 μg O_3 m^{-3} was associated with an increase in visits of 0.31% (95% CI, 0.27%–0.35%) and, when concentrations were between 100 and 160 μg O_3 m^{-3} the increase in visits was 0.43% (95% CI, 0.36%–0.50%). The authors reported that $PM_{2.5}$, PM_{10}, NO_2, SO_2, and CO were not significant confounders. Admissions were significantly greater on warm (daily mean temperature > 18.5°C) than cool days (< 18.5°C), most likely because of correlations between temperature and concentration of O_3.

Effects on the reproductive system. Other studies have shown linkages between exposure to air pollutants and reproductive function. A study on in-vitro fertilization in France showed a reduction in the success of stimulated production of eggs in association with prior acute exposures to NO_2 or PM_{10}.[23] Interestingly, exposure to greater concentrations of O_3 for between 1 day to 2 months before folliculogenesis resulted in enhancement of egg production and successful fertilization. A study on 13,775 pregnancies in North-East Scotland showed that greater annual mean exposure increments of PM_{10} (10 μg m^{-3}), $PM_{2.5}$ (5 μg m^{-3}), and NO_2 (10 μg m^{-3}) were associated with smaller newborns.[32] Exposure to O_3 was not included in this study. A study on birth-weight of 8,948 newborns (2012–2013) in Sao Paulo (Brazil) showed that exposure to elevated concentrations of O_3 in the 30- and 90-day prenatal window was associated with low birth-weight in both sexes (OR = 1.39, 95% CI, 1.05–1.85 and 1.49, CI 1.10–2.00, respectively).[48] Exposure to increased concentrations of PM_{10} was associated with a protective effect but only in female newborns. For the 30-day window, concentrations of PM_{10} ranged from 21.7–85.5 μg m^{-3} and for O_3 from 37.9–71 μg m^{-3}. An unrelated study of vascularization of the placenta in the first trimester in low-risk pregnant mothers (229 participants) in Sao Paulo showed that there was a significant decrease in this measure with increasing concentration of NO_2 (40.5 μg m^{-3}, ± Standard Deviation [SD][24] 7.7 μg m^{-3}).[65] There was no association with concentrations of O_3 (8.2 μg m^{-3}, ± SD 1.15 μg m^{-3}). In a study of hypertensive disorders of pregnancy in Florida (USA), the odds of this condition were reported to be increased by each 10 μg m^{-3} increment in weekly averaged concentration of O_3.[69] The study was based on 655,529 pregnancies with conception dates between 2005 and 2007. The ORs were all < 2 and non-significant, except for gestation time > 24 weeks. The authors noted that exposure early in pregnancy was associated with higher ORs for hypertensive disorders of pregnancy. A recent study of preterm births in cities across Ontario, Canada, and exposures to $PM_{2.5}$ showed an increased risk associated with an increased exposure to $PM_{2.5}$ [IQR = 2.6 μg m^{-3}; OR = 1.08 (95% CI = 1.01, 1.15)] in the first trimester.[92] This study also investigated the oxidative potential of the $PM_{2.5}$ collected in the air samplers used to characterize exposures. Oxidative potential was determined from in vitro incubation of particles with glutathione or ascorbic acid. Consumption of these reactants was used to estimate oxidative potential, which, across 32 cities ranged from 0.01 to 0.36% depletion of glutathione per μg of $PM_{2.5}$ and 0.03 to 0.4% depletion of ascorbic acid per μg of $PM_{2.5}$. When oxidative potential was included in the exposure estimate for $PM_{2.5}$, the above OR increased to 1.31 (CI = 1.07, 1.61) and 1.12 (CI = 0.95, 1.32) glutathione and ascorbic acid, respectively. These results point out the need to characterize the chemical properties of atmospheric particulates when conducting epidemiological studies, as mentioned above when considering PM composition.

24 Standard Deviation [SD], a measure that quantifies the amount of variation or dispersion of a set of data values.

A study in the USA examined risk of stillbirth in a retrospective cohort of 223,375 single-baby deliveries from 12 clinical sites.[125] Based on an interquartile increment in exposures, O_3 was significantly associated with stillbirth (RR = 1.13–1.22) on days 2, 3, and 5–7 prior to delivery (range of IQRs = 35.4–35.6 μg m^{-3}). Relative risk for the whole pregnancy was 1.39 (95% CI, 1.05–1.84). No significant increases or decreases in risk were observed for NO_2, PM_{10}, and $PM_{2.5}$ but a significant decrease in RR (0.80, 95% CI, 0.66–0.96) was observed in the first trimester for SO_2 (IQR = 7.7 μg m^{-3}). Based on these data, the authors suggested that 8,000 stillbirths per year in the US might be attributable to increased exposure to O_3.

A study in the USA assessed the effect of air pollution on erectile dysfunction (ED) in men aged 57 to 85.[171] The 412 participants were from the National Social Life, Health, and Aging Project and daily concentrations of air pollutants were obtained from models ($PM_{2.5}$) and measurements (NO_2, all year [IQR for the 7 years ranged from 13.6–14.9 μg m^{-3}] and O_3, in the summer only [IQR for the 7 years ranged from 13.6–16.4 μg m^{-3}]). Based on an increase of concentrations averaged over 1–7 years, ORs for ED were > 1 but < 2 for all pollutants. None of the ORs were statistically significant. No ED-specific mechanism was investigated or proposed.

Other health effects. The incidence of Parkinson's disease has been associated with air pollutants in a critical review.[140] The strongest linkages were with air pollutants related to traffic and urbanization (NO_2, NO_x, and CO). However, inconsistent (positive and negative) associations between Parkinson's and O_3 were reported in this meta-analysis.

An increased incidence of dementia associated with air pollutants has been reported. A study population of 2.1 million individuals from Ontario, Canada was identified in 2001 and followed to 2013.[26] Historical long-term exposures to $PM_{2.5}$, NO_2, and O_3 were estimated with the aid of satellite observations, a land-use regression model, and an optimal interpolation method. The authors reported a positive association between dementia and $PM_{2.5}$ (HR of 1.04; 95% CI = 1.03–1.05) for every 4.8 μg m^{-3} (IQR) increase in concentration. For NO_2, the HR was 1.10 (95% CI = 1.08–1.12; IQR = 27 μg m^{-3}) but, for O_3 (IQR = 12.6 μg m^{-3}), there was no significant association. The authors estimated that 6% of the cases of dementia were attributable to poor air quality ($PM_{2.5}$ and NO_2). A similar observation for the association of an increased incidence of dementia with exposure to NO_2 was reported in a smaller study from Sweden (1,721 participants).[8] Changes in the human brain associated with PM exposure have been reported.[145] Magnetic resonance imaging (MRI) of the brain in 1,753 individuals in Maryland, Minnesota, North Carolina and Mississippi were compared as a function of exposure to PM_{10} and $PM_{2.5}$ in three time periods (1990–1998, 1999–2007, and 1990–2007). Higher past exposures to PM were associated with smaller deep-gray brain volumes[25].

Impaired physical function has been associated with air pollution. In a study of 1,762 Dutch older (75 ± SD 9 years) adults,[39] data were collected between 2005–2006, 2008–2009, and 2011–2012 on performance-based activities (walking speed, ability to rise from a chair, putting on and taking off a cardigan, and a balance-test). An association in decreased performance and NO_2, NO_x, $PM_{2.5}$, and PM_{10} was reported (IQRs of 8.9, 13.5, 1.4, and 1.5 μg m^{-3}, respectively). Significantly decreased performance was observed only for the upper exposure quartile for NO_2 (> 43 μg m^{-3}), NO_x (> 67 μg m^{-3}), and PM_{10} (> 29 μg m^{-3}). The authors noted that the decrease in score resulting from exposure to air pollutants was equivalent to an increase in age of nine months. A large-scale study (75,000 people) in China,[199] reported that exposure to air pollutants was associated with decline in cognitive ability in terms of verbal and mathematical tests in

25 Smaller deep-gray brain volumes are characteristic of Alzheimer's disease.

adults ranging in age from 25 to 65+ years. Air quality was measured using the air pollution index, a composite of daily concentrations of SO_2, NO_2, and PM_{10}, obtained from the city-level air quality reports for 86 major cities in 2000 and most of the cities in China in 2014. Because of the use of the composite, it was not possible to attribute a response to a specific chemical pollutant. Collectively, these studies show that exposures to air pollutants can result in non-lethal effects that significantly affect quality of life, especially in the elderly.

Increased concentrations of ambient O_3 were reported to be associated with increased risk of Type-2 diabetes.[78] This study used data from a cohort of 45,231 African American women from 56 cities across the USA. Concentrations of O_3 were estimated using modeled predictions adjusted with ground measurements from 2007–2008. For an interquartile increment in concentration of O_3 of 13 $\mu g\ m^{-3}$, a significant increase in incidence of 1.18 (95% CI, 1.04–1.34) of Type-2 diabetes was reported. This appeared to be specific to O_3 and was not associated with $PM_{2.5}$.

Overall, air pollutants in general have very significant and diverse effects in humans. In general, fine particulates ($PM_{2.5}$) are most important, but O_3 and NO_2 are also relevant for some outcomes. Ozone appears to not be associated with an increased frequency of dementia, an important condition in the elderly, but other air pollutants are, particularly PM, where direct effects also have been observed on the brain. Future changes in health impacts will depend on changes in UV radiation and the UV-induced changes in pollutant concentrations, as well as changes in emissions and climate.

4.2 Future changes in human health due to climate

Future climate change has been estimated to produce significant changes in air quality as measured by exposure of humans to O_3,[42, 77] with actual exposure dependent on a range of factors. While this study was based on modeling changes in demographics of humans, it assumed that human behaviour will not respond to changes in climate. Further, it did not attempt to capture changes in local emissions due to changing air quality. As has been pointed out, there is considerable background variability in concentrations of ground-level O_3.[52] Thus, detecting trends in air quality data due to climate changes will probably require longer-term datasets (> 15-years) with averaging times currently used.

Climate change on its own is predicted to directly change the incidence of heat-waves with consequences for humans.[163, 176] A study based on historical data on deaths in New York City related to increased temperature predicted that a range of responses could occur.[143] Based on the response of the population to greater temperatures in the last 80 years and predictions from 33 climate-change models, the authors suggest that, for the IPCC Representative Concentration Pathway (RCP) 4.5, annual mortality would decrease from 638 heat-related deaths between 2000 and 2006 to 167 in the 2080s (June – September). This is driven by high adaptation and assumed demographic change. However, for RCP 8.5, the estimated annual number of deaths was estimated to increase to 3,331 with minimal adaptation.[143] In addition to increased mortality, decreased and increased temperatures resulting from climate change are predicted to boost demand for medical services. This has been reported for developed-[50, 109] and developing-countries.[203] In the latter case, a study in China reported that, in 2011–2014, north-south variations in effect of temperature in admissions to emergency departments were observed but admissions were greater at temperatures below the average than at temperatures above average.

Interactions between effects of air pollutants on humans and climate continue to be observed. The association between concentrations of O_3 and general mortality, cardiovascular, and respiratory mortality in Zhengzhou, China were observed to be more pronounced in the cold than in the summer months.[149] Daily mean temperature and relative humidity were 23.9°C and 57% in the warm season and 8.2°C and 52.8% in cold season, respectively. The association between atopic dermatitis in children in Korea and increases in tropospheric O_3 and other atmospheric pollutants was weaker with greater outdoor and relative humidity.[87] A study on the interactions between climate change and future concentrations of tropospheric O_3 suggested differences between two RCPs.[168] For RCP 4.5, predicted increases in the concentration of O_3 for the 2050s from a combination of climate change and emission control policies was estimated to result in a small increase in annual premature deaths (50) in the USA. For RCP 8.5, predicted increases in concentrations of O_3 were estimated to result in over 2,200 additional premature deaths annually by the 2050s. A similar projection to 2025–2035 of concentrations of O_3 and temperatures in cities in the USA suggested that mortality attributable to O_3 > 80 μg m^{-3} would increase by 7.7% (95% CI, 1.6–14.2%).[183] Mortality from concentrations of O_3 > 150 μg m^{-3} was predicted to increase by 14.2% (95% CI, 1.6–28.9%). Increases in concentrations of O_3 and interactions with climate change are predicted to result in increased mortality and morbidity.

4.3 Adverse effects of poor air quality on vegetation, crop plants, and food security

The effects of air pollutants on vegetation, particularly increased concentrations of O_3, have been assessed in previous reports[12, 176] and these effects continue to be important. While concentrations of PM_{10} and $PM_{2.5}$ appear to have few effects on plants, the effects of increased concentrations of O_3 continue to be documented, impacting the production of crops and the yields of fibre and food for humans and domestic animals. Forests store the largest terrestrial pools of carbon and contribute to the stabilization of the global climate system. However, forests are threatened by climate change and associated air pollution, such as O_3 and NO_x.[122] There are possible negative feedbacks in this system as O_3 tends to counteract stimulation of plant-growth by elevated concentrations of CO_2.

Sensitivity to ambient and above-ambient concentrations of O_3 continues to be reported for distinct species of vegetation (**Table 2**), although some photosynthetic organisms have been shown to be insensitive to O_3. Chlorolichens, for example, possess antioxidant systems that are highly expressed because of their need to tolerate very variable water-stresses (poikilohydric).[15] These antioxidant systems were shown to protect two species of lichen (*Parmotrema perlatum* and *Xanthoria parietina*) from exposures to 500 μg O_3 m^{-3} for 5 h per day for 14 days. Lichens are important in food chains for Arctic caribou but Arctic regions are estimated to rarely experience ground-level concentrations of O_3 > 80 μg m^{-3},[10] so food chains in the Arctic are unlikely to be adversely affected by transport of O_3 to the lower troposphere.

Table 2 **Reports of adverse effects observed in plants after exposure to ozone in semi-field experiments, where plants are exposed to ozone in partially open experimental chambers.**

Species of plant and adverse effect observed	Exposure to ozone		Reference
	Conc. (μg m^{-3})	Time of exposure	
Larix kaempferi and *L. gmelinii* var. *japonica* cross *L. kaempferi,* (discolouration of leaves, reduced concentration of chlorophyll, and height of plants)	132	2 years	Ref.[4]
Oryza sativa (rice, var. Nipponbare, L81, and BRRI dhan28), (reduced height and tillering, stomatal conductance, lipid peroxidation, biomass, and yields)	154	5 weeks after transplant to harvest	Ref.[11]
Triticum aestivum (wheat, var. Yannong 19, Yangmai 16, Yangmai 15, Yangfumai 2, and Jiaxing 002), (decreased photosynthesis)	104	7 h per day from tillering to harvest	Ref.[47]
Cryptomeria japonica (no effect on growth and photosynthesis, increased height increments in year-one)	66	10 h per day for 194 and 208 days over two years	Ref.[67]
Sixty species of woody plants from temperate and subtropical regions of China, (reduced biomass of woody plants, reduced photosynthesis and transpiration, reduced chlorophyll content, growth)	232	Variable	Ref.[101]
Ficus insipida tropical tree from Panama (downregulation of secondary metabolites, accelerated senescence of leaves).	60 (ambient)	Max. ambient value, duration not reported	Ref.[156]
Lactuca sativa (lettuce var. Romana and Canasta), (reductions in yield but differences between cultivars)	130 (filtered)–212 (ambient)	24 h for 22–34 days	Ref.[121]
Populus deltoids and *P. euramericana* (clones), (changes in concentrations of carbon, nitrogen, phosphorus in different "organs" of the plants)	120	10 h per day for 96 days	Ref.[161]
Plantago major and *Sonchus oleraceus* (reductions in the light-saturated net photosynthesis, stomatal conductance, and transpiration rate)	170	9 h per day for 30 days	Ref.[169]
Zea mays (maize, 18 diverse maize inbred and hybrid lines), (accelerated senescence of leaves with variation between lines)	200	8 h per day for 62–75 days in three seasons, 2013–2016	Ref.[187]
Machilus ichangensis and *Taxus chinensis* (subtropical trees from China), (reduced rate of photosynthesis, changes in biomarkers of oxidative stress)	300	8 h per day for 245 days	Ref.[192]

Further estimates of decreased yields in important crops due to exposure to O_3 have been reported. In a study of production of rice in China,[24] it was shown that, for each day with concentrations of O_3 > 240 μg m^{-3}, there was a loss of yield of 1.12% ± 0.83%. The authors point out that increased concentrations of O_3 at ground-level in China may lead to reductions in rice yields large enough to have implications for the global rice market. A study of concentrations of O_3 in the delta of the Yangtze River during the growing season for rice and wheat reports significant losses.[202] In 2015, the estimated loss of yield was 10–36% for wheat and 7–24% for rice, estimated by the authors to be equivalent to losses of 2.1 and 2.4 billion US$ respectively. Similar conclusions were drawn in an extensive survey of concentrations of NO_x (a precursor of O_3) in India and their potential effects on yields of wheat and rice.[162] Overall, there is compelling evidence that many species of plants can be adversely affected by O_3 and that

this results in economically significant losses in yields. These points need to be considered in decision-making in response to future changes that are expected to result from changes in stratospheric O_3, tropospheric air pollutants and climate change.

Some advances have been made in terms of monitoring the effects of O_3 on plants. It had been suggested that yields of O_3-sensitive and O_3-tolerant genotypes of snap bean (*Phaseolus vulgaris* L.; S156 and R123) could be used for biomonitoring of ambient O_3. However, a study conducted in outdoor plant environmental chambers in Greece showed that yields were also sensitive to temperature in both strains but with a difference in response.[2] Similar effects of local climate were observed in studies on clover (*Trifolium subterraneum* and *T. striatum*) exposed to O_3 in Spain;[57] however, here the authors suggested that Phytotoxic Ozone Dose (POD), based on the accumulated O_3 flux into the leaves, was a more accurate indicator of damage. A review of the use of reflectance spectroscopy to monitor responses of plants to air pollutants suggested that this was a reliable technique for assessing damage in leaves from exposure to O_3 and several other air pollutants.[36] The influence of local temperature and water stress (see below) on the effects of O_3 is potentially important in relation to the interaction of climate change with exposure to O_3 in plants.

Several interactions between tropospheric O_3, biological processes, other stressors, and nutrients have been reported in the literature. Exposure of birch (*Betula platyphylla* var. *japonica*) to above-ambient concentrations of O_3 resulted in decreased feeding by leaf-beetles *(Agelastica coerulea)*,[153] but this response was not observed in another study on the same tree for the same beetle.[3] The reason for this inconsistency is not clear. Plants have been reported to respond to exposure to O_3 by increasing the production and release of antioxidants.[17] These defense compounds include several volatile chemicals, such as geranyl acetate, α-cadiene, trans-farnesol, cis-β-farnesene, which might indirectly contribute to air pollution. The concentration of O_3 was high (200 μg m^{-3}) so the relevance of this to lesser exposures is unclear. When stressed, many plants emit BVOCs, which can be used by other nearby plants to "gain information" that is used to adjust their own defenses. Using cabbage (*Brassica oleracea* var. *capitata*) as a test species, Giron-Calva *et al.*[54] showed that exposures to elevated concentrations of O_3 (100–120 μg m^{-3} compared to a background of 40 μg m^{-3}) impaired the plant-to-plant signaling, thus potentially exacerbating damage by herbivores.

Drought can interact with plant responses to exposure to O_3. In a study on the Mediterranean oak, *Quercus ilex*, damage from acute (5-h) exposure of 400 μg m^{-3} O_3 differed between well-watered and water-deprived plants.[35] The normal response to O_3, such as release of phytohormones and signaling molecules, ethylene, abscisic acid, salicylic acid, and jasmonic acid, were observed in watered plants but not in water-deprived plants. Thus, interactions between tropospheric O_3 and drought are likely to decrease protective responses in plants and make them more susceptible to damage from O_3 alone. Another study on the same species of oak showed that exposure to salt (NaCl) via soil decreased protective responses to a 5-h exposure to O_3 at 160 μg m^{-3}.[58] Others have shown opposite effects where other stressors mitigated the effects of O_3 on plants. Water stress in an O_3-sensitive hybrid poplar clone '546' [*Populus deltoides* cv. '55/56' crossed with *P. deltoides* cv. 'Imperial'] was protective against exposures to 80 μg m^{-3} O_3.[51] Exposures in this study were for 9 hours per day and lasted for 96 days during the summer months. In a study on the Chinese ornamental tree, *Lonicera maackii,* exposures to 160 μg O_3 m^{-3} and water restriction increased the production of bioindicators of stress but decreased visible injury on leaves.[186] In soybeans *(Glycine max)*, exposures to 80 μg O_3 m^{-3} for 50 days caused a reduction in conductance of water in whole plants,[198] suggesting adverse interactions between exposure to O_3 and water-stress.

Reduced availability of zinc, an essential nutrient for plants was protective for damage by O_3 in seedlings of durum wheat *(Triticum turgidum subsp. durum)*.[38] Exposures were acute (4-h) at a large concentration of 300 μg m^{-3}, conditions that are not common. In another study, exposure of bamboo (*Phyllostachys edulis* and *Oligostachyum lubricum*) to 100 μg O_3 m^{-3} for 10 h per day for 112 days reduced uptake and distribution of mineral nutrients (nutrient (Ca, Mg, and Fe) in the plants.[206] No interactions, positive or negative, were observed in saplings of silver birch *(Betula pendula)* to 24-h mean concentrations of O_3 ranging from 72 to 136 μg m^{-3} (for 165 days in the first year and 122 days in the 2nd year) and four rates of nitrogen fertilizer (10, 30, 50, or 70 kg N ha^{-1} y^1).[61] Similar lack of interactions were reported in another study on inhibition of isoprenoid-biomarkers of exposure to 80 μg O_3 m^{-3} in Cathay poplar *(Populus cathayana)* treated with nitrogen fertilizer at 50 or 100 kg N ha^{-1} y^1.[193] In soybean *(Glycine max)* interactive effects were found from exposure to enhanced UV radiation (5% increase in UV-B and UV-A radiation over ambient) and O_3.[120] Plants were exposed to O_3 at a mean concentration of 90 μg m^{-3} for 8 h d^{-1} for 53 days. Both the number of seeds and mass of seeds per plant were significantly reduced for the combination treatment compared to the UV radiation or O_3 alone; however, the design of the study did not allow differentiation of additivity and synergism. Studies of the interactive effects of O_3 and other stressors are relatively few and reported results are not always consistent. A better understanding of these mechanisms would be useful in developing regulatory policies for better protection of crops from the effects of O_3 and changes in climate.

Tolerance to tropospheric O_3 in plants has been identified as a pathway to reducing the effects of air pollutants on the economic and yield benefits of crops important to humans.[5] In a number of cases, quantitative trait loci for tolerance to O_3 have been identified in model and crop plants; however, as has been pointed out *"there is considerable research to be done before O_3-tolerant germplasm is available to growers for most crops"*.[5] Development of these traits has been *"hampered by the lack of translation of laboratory experiments to the field, and the lack of correlation between visual leaf-level O_3 damage and yield loss to O_3 stress"*.[5]

In a meta-analysis of the interactions between arbuscular mycorrhiza (beneficial fungi that colonize roots of plants and facilitate uptake of nutrients, such as phosphorus) and O_3, it was reported that colonization by arbuscular mycorrhiza offered protection against O_3.[179] Regardless of species of fungi, colonization by arbuscular mycorrhiza had little effect at exposures up to 160 μg m^{-3}, but did confer protection at greater concentrations, even though rates of colonization were reduced by longer time of exposure to O_3. This observation suggests that arbuscular mycorrhiza could be used as a tool to protect crops against adverse effects of O_3.

With the increasing dependence on genetically engineered (GE) crop plants, care should be taken to avoid compromising resistance to pollutants such as O_3 when other traits are inserted into the genome. A study on the effects of elevated O_3 on conventional and GE-rice showed a greater loss in yield from the variety engineered to express the insecticidal gene for Bacillis thuringiensis endotoxin, Bt Shanyou63 (Bt-SY63) compared to its non-GE counterpart Shanyou63 ($SY63_3$).[98] Plants were exposed for 91 days, but exposure was variable and time-weighted mean concentrations or cumulative load above AOT40 were not provided. A graphical display showed concentrations in the treatment enclosures ranging from 0 to 250 μg m^{-3} and AOT40 values as large as 1500 μg m^{-3} h.

5 Emissions to the atmosphere relevant to the Montreal Protocol

Most emissions of relevance to air quality are either not manageable (e.g., emissions from vegetation) or are managed by local authorities (e.g., tailpipe emission standards for internal combustion engines) rather than by international agreements like the Montreal Protocol.

The substances that replaced those initially regulated by the Montreal Protocol may contribute to poorer air quality. One of the advantages of chlorofluorocarbons (CFCs) was that they were inert in the lower atmosphere and had no direct impact on air quality. Their replacements have been specifically chosen to be less stable, and hence may be important for air quality. As these compounds are directly relevant to the implementation of the Montreal Protocol, their impacts on air and environmental quality need to be considered. Focusing on refrigeration, these replacements include ammonia, hydrocarbons, hydrofluorocarbons (HFCs) and hydrofluoroolefins (HFOs). Carbon dioxide is not discussed as a refrigerant, as it is unlikely that any release from uses of relevance to the Montreal Protocol will have direct adverse effects on human health, the environment, or food-security. Because of the way they are used, refrigerants regulated under the Montreal Protocol will eventually be recovered or released to the atmosphere where they will either degrade or cause adverse effects on stratospheric O_3. While it has been suggested that HFOs might become relevant pollutants in groundwater,[73] this is inconsistent with their properties. Given the physical and chemical properties of the fluorinated refrigerants (low solubility in water, large air-water partition coefficients, and short half-lives in the troposphere), they will not partition into surface- or ground-waters in biologically relevant amounts.[178] If the alternative refrigerant, ammonia, is released to the atmosphere it will dissolve in water droplets and could enter surface water via precipitation, where it might cause toxicity to aquatic organisms, especially fish.[18]

5.1 Trifluoroacetic acid from replacements of ODS and refrigerants with large GWPs

Trifluoracetic acid (TFA) is a persistent substance that is formed in the atmosphere from several HCFCs, HFCs, and HFOs, the use of which falls under the purview of the Montreal and Kyoto Protocols, and their Amendments. When released into the atmosphere, several of these gases react with the hydroxyl radical (OH) to form TFA as a terminal residue.[164] The fate of TFA in the environment (illustrated in **Fig. 11**) and its potential effects on humans and the environment have been discussed in most of the reports of the EEAP, including the last Quadrennial Assessment Report[117] and the Update Reports since then[12, 175, 176] and the reader is referred to these. In the critical review and risk assessment on the fate and effects of TFA in the environment,[164] conservative estimates of production and release of precursors were used so that the estimated additional inputs of TFA to the global environment are an upper-bound. The following is a summary of recent findings and a perspective on the relevance of the formation of TFA in the environment.

Previous reports[12, 164, 176] have consistently noted that TFA is very recalcitrant to breakdown in the environment. This finding still holds true. A new report confirmed the catalytic defluorination of TFA in the presence of electrolysed sulfuric acid ($S_2O_8^{2-}$) and UV radiation[115] but this is unlikely to occur in nature and the energy requirements in laboratory conditions are too large to be practical for decontamination of water. Reductive defluorination of long-chain perfluorinated compounds can be catalysed by natural and anthropogenic compounds

containing cobalt.[113] This study did not report defluorination of TFA but the conditions for these reactions are unlikely to be found in the environment.

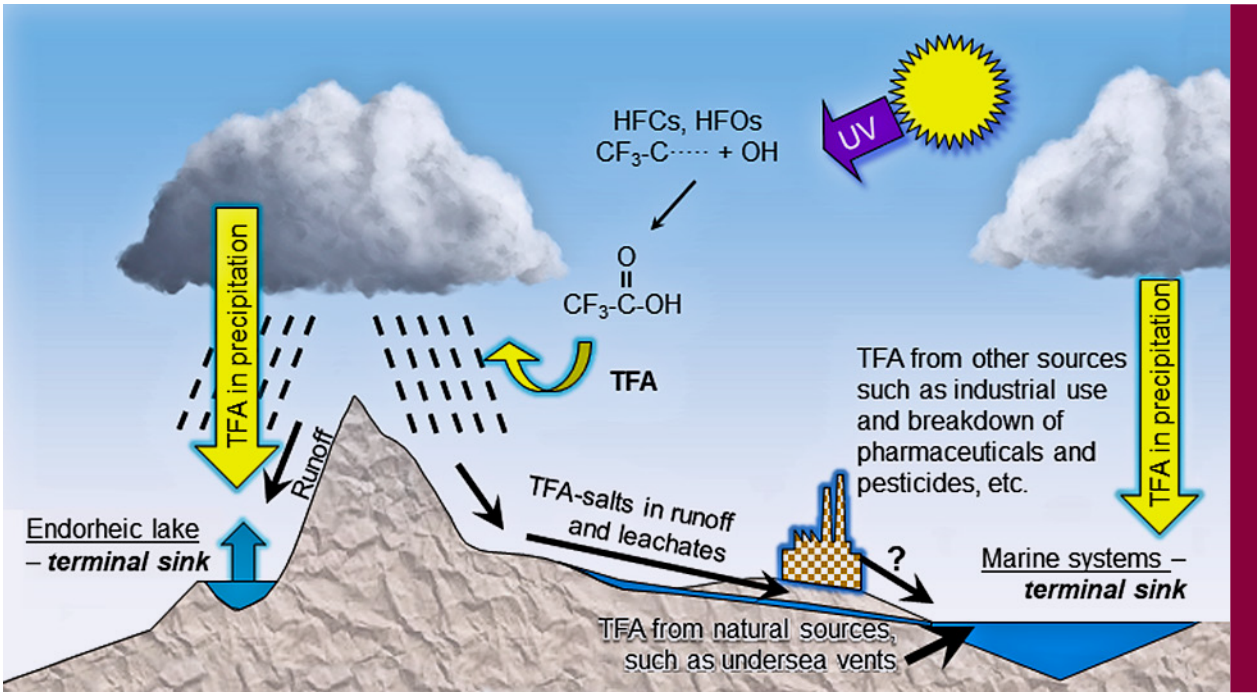

Fig. 11 **Trifluoracetic acid (TFA) formed from HFCs and HFOs in the atmosphere will rapidly partition from air to water in the atmosphere. It will combine with cations in soil and surface water and accumulate in endorheic water bodies (salt lakes) and the oceans. TFA produced from HFCs and HFOs can be reasonably well quantified but this is not true for natural sources and other chemicals used by humans (modified from ref.[164], with permission).**

Experiments with microbiota isolated from samples collected from a site with a long history of industrial contamination and activated sludge obtained from a municipal wastewater treatment plant showed that TFA was recalcitrant to biologically-mediated degradation.[155]

Other than the HCFCs, HFCs, and HFOs, there are many other sources of TFA in the environment. Because of its resistance to decomposition, it is likely to be the end-product remaining after the metabolism and environmental degradation of some 1.4 million compounds which contain the C-CF_3 moiety. While many of these compounds are likely produced in small quantities, there are virtually no data on global production and release to the environment. The use and release of refrigerants and blowing agents is documented under the Montreal and Kyoto Protocols, thus making it possible to estimate the historical, current, and future contribution of these sources to environmental loadings of TFA. The future use of precursors of TFA that are regulated under the Montreal Protocol will change in response to the Kigali Amendment but how these changes will affect future use and release of these compounds is still unknown (Velders, G, pers. comm., Jan 15, 2018).

Inputs of TFA into the environment from future conversion of all mobile (mainly automotive) air conditioners (MACs) to HFO-1234yf in China, the USA, and Europe have been estimated using a global 3-D chemical transport model,[180] extending and confirming previous modelling for North America.[114] This modelling highlights the variability in transport globally from these

sources. However, the limited emission inventory, uncertainties in the chemical degradation pathway,[29] and very limited hazard assessment restricts the usefulness of these results in a global assessment. Because the HFCs that can break down in the atmosphere to produce TFA have long half-lives (1–100 years),[76] they can be distributed globally before significant degradation occurs. Thus, the formation of TFA from these HFCs is distributed globally rather than locally. The half-life of the newly introduced refrigerant, HFO-1234yf, is much shorter, of the order of 11 days,[134] thus, breakdown will occur closer to the regions of release and larger concentrations of TFA would be expected in surface waters.[83, 114, 180] In assessing risks from local deposition of TFA, it is important to note that TFA will form neutral salts once in contact with soil and/or surface waters. For example, from the estimates of production of TFA in China, the USA, and Europe[180] and assuming no dilution, this would be equivalent to 761, 573, and 740 ng Na salt L^{-1}, respectively, all of which are still several orders of magnitude less than the chronic "no observable effect concentration" (NOEC) of 10,000,000 ng L^{-1} for TFA-Na salt from a microcosm study.[59] Although the authors point out that concentrations in precipitation in arid regions would be greater, TFA salts would run-off into the ocean where they would be diluted or accumulate in endorheic bodies of water where environmental effects of other mineral salts, which are present in much greater concentrations, outweigh those of TFA salts.[164] Overall, there is no evidence to suggest that these local depositions of TFA will result in risks to the environment, especially when eventual dilution in the oceans or endorheic bodies of water occurs. A recent review of this topic[135] reached similar conclusions with respect to TFA formed from HCFCs, HFCs, and HFOs.

Occurrence of TFA in dry-deposition from air near two landfills (Shuangkou and Baodi) in Tianjin, China[173] suggests TFA was produced from sources other than HCFCs, HFCs, and HFOs. However, it is most likely that TFA found in air, cloud- and fog-water, rainfall, and snow is the result of breakdown of precursors regulated under the Montreal and Kyoto Protocols (**Fig. 11**). Once precipitation reaches the surface and mixes with surface waters, there are many other unidentified and unregulated substances that could be precursors.[155] To regulate all these potential precursors would present a very large global challenge.

There is still no indication that exposure to current and projected concentrations of salts of TFA in surface waters present a risk to the health of humans and the environment. Since the risk assessment conducted in 2016, no novel studies indicating adverse long-lasting effects of TFA and its salts have been published. In fact, the reverse is true. Previous reports of contact toxicity from exposure to concentrated TFA (as a strong acid used in industry) have not indicated systemic toxicity.[37, 170] TFA in rain-water is millions of times more dilute than that in industrial solutions and would not cause adverse effects.

5.2 Hydrocarbons

Among the replacements for ozone depleting refrigerants are hydrocarbons. The release of hydrocarbons (such as propane and n-butane) from refrigeration systems will add to the burden of hydrocarbons in the atmosphere, and potentially increase the concentration of O_3 following atmospheric decomposition (see **Fig. 3**). Given that the atmospheric lifetimes of these hydrocarbons are of the order of 1–2 weeks,[63] formation of O_3 following their release (**Fig. 3**) will occur over national to continental distances. The assessment of the impact of emissions of hydrocarbon refrigerants on air quality in the refereed literature is limited.[177] A more comprehensive estimate has been made for three cities in the USA in a consultancy report.[88] These cities were chosen because of the problems they face with pollution by O_3. The estimates of a "worst case" increase in O_3 (as measured by the maximum increase in

the 8-hour average) is around 13 μg m^{-3}, but a realistic estimate of 0.3 μg m^{-3} (for reference, the ground level 8-hour regulatory standard for O_3 is 140 μg m^{-3} in the USA). This highlights significant uncertainty and the need for some caution in the implementation of these hydrocarbon refrigerants to avoid the "worst case" situation.

5.3 Ammonia

Ammonia (NH_3) has been used for over a century as a refrigerant, particularly in larger (industrial) installations. In the USA, which has a Hazardous Substances Emergency Events Surveillance (HSEES) system for the nine states of Colorado, Iowa, Minnesota, New York, North Carolina, Oregon, Texas, Washington, and Wisconsin, NH_3 was the most commonly released chemical involved in single chemical incidents reported for the years 1999–2008, involving some 3366 incidents.[139]

Ammonia presents a significant problem for air quality. Besides refrigeration there are several large biogenic and combustion sources of NH_3 that appear not to be well quantified. Ammonia in the atmosphere reacts with several compounds to produce aerosols and hence increase concentrations of $PM_{2.5}$. There are large improvements in air quality that could be made through the limitation of emissions of NH_3, and it seems likely that this will lead to tighter emission controls from all managed sources.[146] However, use of NH_3 as a replacement refrigerant would represent only a small fraction of current emissions. Full replacement by NH_3 of current emissions of CFCs, HCFCs, and HFCs, estimated to total 170,000 tonnes yr^{-1} (for 2017; G. Velders, pers. comm., Feb. 2018), would be small compared to estimated emissions of NH_3 of 34,500,000 tonnes yr^{-1} from agriculture,[16] or 8,500,000 tonnes yr^{-1} from industrial and residential activities.[126]

6 Knowledge Gaps

UV radiation, and specifically UV-B radiation, provides much of the energy for both the generation and removal of many air pollutants. However, the multitude of pollutant sources and the importance of external factors such as temperature and wind, tend to mask the sensitivity of air quality to UV radiation. While the basic chemical mechanisms behind UV-driven generation of pollutants are well understood, quantifying the impact of stratospheric ozone changes on air quality remains a significant challenge. Changes in climate will also have a significant impact on air quality, not only through changes in temperature, wind, and rain in the lower atmosphere but also through potential changes in transport of stratospheric ozone to the troposphere. This transport remains poorly characterized by both models and observations.

A critical component in predicting changes in the global atmosphere is to constrain the likely changes in the key chemical oxidants, especially the OH radical. However, while techniques to measure OH locally are now well established, there is still no consensus on the trend in global OH concentration in the recent past, and this is a prerequisite to having confidence in future predictions.

There have been significant advances in relating air pollutants to human health recently through the study of very large populations. These techniques are most useful for acute impacts, and more chronic effects remain a challenge to quantify, given the multitude of changes people are experiencing over a lifetime. Further, some of the measures of air quality are, in themselves, limited. The use of $PM_{2.5}$ as a measure of the aerosol loading that is relevant

to human health remains debatable. Beyond the question of the size of particles, the impact of the chemical composition of aerosols on human health remains unclear. While there is good reason to expect a relationship between aerosol composition and health, the framework for studying this has yet to be developed.

7 Conclusions

Photochemically-produced O_3 and secondary particulate matter near the ground are well established as major environmental threats to human health, with of the order of 3 million deaths per year ascribed to poor air quality (Table 1). Emissions of precursors for O_3 and particulate matter (particularly VOCs and NO_x) will continue to be the major driver of poor air quality. UV radiation (particularly UV-B), provides most of the energy to drive the formation of O_3 and particulates in the atmosphere. Because of the Montreal Protocol, past and future changes in UV radiation at ground level are relatively small (outside Antarctica), so that the relative effects of actions under the Montreal Protocol on air quality are expected to be small. However, even a small relative change in UV radiation (e.g. 1%) could be of major importance given the already large number of people affected by poor air quality.

Ozone can be transported from the stratosphere down to the biosphere under certain meteorological conditions. While this has been long recognized, quantifying the magnitude of this transport remains difficult. While the amount of O_3 reaching the earth's surface is small, it represents a significant source for O_3. Future recovery in stratospheric O_3 concentrations as well as an increase in vertical mixing due to climate change will change the amount of O_3 reaching the Earth. These changes have the potential to increase the amount of O_3 reaching the surface from the stratosphere, thereby increasing the probability of air pollution events that adversely affect humans and the environment.

Trends in the concentrations of O_3 at the surface depend on geographic location and are affected by changes in UV radiation. The long term (20+ year) trend in surface O_3 depends heavily on the emissions of key precursors (volatile organic compounds and nitrogen oxides). Locations where emission controls have made a significant impact have shown decreases in surface O_3. However, in regions where economic growth drives emissions, there has been an increase in concentrations of O_3. The recovery of stratospheric O_3 will lead to a decrease in the UV radiation in the troposphere. This will lead to a small decrease in O_3 in large cities but an increase in O_3 outside these major source regions, potentially increasing the O_3 concentration to which the population is exposed.

UV-driven photochemical reactions convert volatile compounds into non-volatile products, leading to the formation and growth of many particles. While the overall process is generally understood, the details and the impact of changing UV radiation on the amount of PM in the atmosphere is still not well characterized.

Exposure to fine particulates ($PM_{2.5}$) and O_3 has been associated with diverse and very significant adverse effects in humans. PM have been associated with more causes of morbidity and mortality than is the case for O_3 and, in general, are an order of magnitude more important for adverse effects on human health. Ozone has only been associated with mortality from acute respiratory distress, cardiovascular disease, still-birth, and morbidity for conditions such as cough, hypertension, type-two diabetes, and Kawasaki disease.

One of the major difficulties in interpretation of studies on the effects of air pollutants on humans is the characterization of actual exposures. Models are often used to translate PM

amounts at locations where measurements are made to locations where people live. These measurements are often based on average values and individual exposures will typically vary more than the estimated values. Despite this variability, many associations are still significant, suggesting that better estimates of exposure for individuals might provide more robust evidence of the effect of PM on health. A second source of uncertainty is the almost complete lack of knowledge of the composition of PM to which humans are exposed. Classification of particles based on size (PM_{10} or $PM_{2.5}$) does not consider the chemical composition of the particles or their biological potency. Particles have been shown to contain metals, inorganic compounds, and a wide range of organic substances. Characterization of the composition of PM in atmospheric monitoring, as has been done in very few instances, and their variation over time and location, would be useful in understanding causality and could then potentially lead to better protection of human health.

There is compelling evidence that many species of plants are adversely affected by elevated concentrations of O_3, which can result in economically significant losses for nutritionally significant crops such as wheat and rice in India and China, where concentrations are generally high. The concentration of O_3 in these regions could increase due to ozone recovery and climate change (as mentioned above). On the other hand, exposure to particulates ($PM_{2.5}$ and PM_{10}) appears to have little direct effects on vegetation, including crop plants.

Interactions between plant metabolism and tropospheric O_3, other stressors, and nutrients have been reported in the literature. Increases in temperature and water-stress have been shown to enhance the adverse effects of O_3 in plants. Studies of the interactive effects of O_3 and other stressors are relatively few and reported results are not always consistent. A better understanding of the impact of exposure to O_3 and mechanisms of interaction with other stressors would be useful in formulating regulatory policies for the better protection of crops from the effects of changes in surface O_3 and climate.

The phase-out of ODSs has led to a range of other chemicals being considered, especially for refrigeration, with the potential for these to be released to the atmosphere. These substances include ammonia, hydrocarbons, hydrofluorocarbons, and carbon dioxide. Ammonia can have a significant detrimental effect on the environment in general, but except at the site of a significant release, the amounts used for refrigeration are small relative to sources such as agriculture. The release of refrigerant hydrocarbons (volatile organics) could have negative impacts on air quality, although current estimates suggest that it is small. Carbon dioxide for this use is unlikely to have an impact on air quality.

Trifluoracetic acid is a highly persistent, terminal breakdown product resulting from the atmospheric degradation of several hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and hydrofluoroolefins (HFOs) that are regulated under the Montreal Protocol (with the Kigali Amendment). Trifluoroacetic acid will dissolve in water in the atmosphere and be deposited on the Earth's surface via precipitation, where it will react with minerals in soil, sediment, and surface water to form salts. These salts of TFA will accumulate in the oceans and the terrestrial water bodies with no outflow (salt lakes). Based on upper-bound estimates of use and release of the HFCs and HFOs in the next 50 years, the addition of TFA salts to the existing natural background concentrations in oceans and salt lakes presents a *de minimis* risk to human and environmental health. It should be noted that TFA is a potential terminal residue of many industrial chemicals, pesticides, and pharmaceuticals, most of which are eventually released into the environment. While past and projected use of HFCs and HFOs is reasonably well understood, the relative contribution of these other industrial sources of TFA to the global load is almost completely unknown and represents a challenge to regulators.

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7 Interactive effects of solar UV radiation and climate change on material damage

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Summary

Solar UV radiation adversely affects the properties of organic materials used in construction, such as plastics and wood. The outdoor service lifetimes of these materials are influenced by their rates of degradation under solar UV radiation as well as by other climate factors such as temperature, moisture, and atmospheric pollutants. While recovery of the stratospheric ozone layer is expected, local increases in UV radiation are still likely to occur, especially in the tropics, but also elsewhere as a consequence of climate change effects. Such increases, when taken together with an increased ambient temperature due to climate change, can significantly shorten the service lifetimes of organic building materials. Several proven technologies, including the use of UV stabilisers, surface treatments or coatings have been developed over the years to mitigate these adverse effects. While these technologies should be able to compensate for any realistic future UV radiation and climate change scenarios, they will also add significantly to the lifetime cost of material in relevant products. Shorter outdoor lifetime of the plastic components in photovoltaic (PV) modules is a serious concern in the solar energy industry. To ensure module durability over the full service-lifetime (of about ~20 years) of the light-harvesting PV components, better stabilisation technologies are being investigated.

The present trend towards more environmentally sustainable materials in building, and environmental impacts of additives such as stabilisers, need to be considered in addition to their engineering performance. This may require the phasing out of some conventional additives used in plastics as well as substituting wood or other materials in place of plastics in buildings. Depending on relative costs of mitigation, substituting more UV-stable materials for conventional ones in outdoor products may also be a viable option with some categories of products. Neither the global cost of mitigation of the effects of climate change on materials nor the long-term sustainability of the technologies available for the purpose, have been estimated.

Plastic waste and litter exposed outdoors to solar UV radiation over extended periods undergo cracking and fragmentation into small pieces (micro- and nano-scale size). Release of these fragments into the environment, particularly in the aquatic environment, poses a potential threat to marine biota. Already several hundred of species are known to ingest these fragments that can potentially accumulate additives and pollutants from water. This is a potential threat to humans because 25% of fish marketed for human consumption have been reported to contain microplastics in their digestive systems.

The focus of this assessment is on recent advances in understanding the mechanisms of UV-radiation-induced degradation in materials and in assessing emerging technologies for their stabilisation against UV-degradation outdoors. Better understanding of the mechanisms of degradation allows for innovative stabilisation approaches to be developed. Also assessed is information on sustainability of the available and emerging UV stabilisation technologies.

1 Introduction

Wood and plastics dominate building construction materials worldwide. A record 900 million cubic meters of bulk sawn wood and wood paneling were produced globally in 2016,[43] amounting to 3% growth over the previous year. Driven by growing economic demand, global manufacturing of wood products has increased consistently over the past seven years. Similarly, plastic resin production increased to 331 million metric tons (MMT) in the same year, with about a third of the production being used in building construction applications. The most common plastic resin used in buildings is poly(vinyl chloride) (PVC) plastic, which is popularly used in a wide range of exterior applications as well as in flooring and membrane roofing. In fact, about 75% of PVC global production of about 41 MMT[142] is consumed by the building industry.

Protecting materials from solar UV radiation, especially the UV-B (280–315 nm) radiation, is important to ensure their long service lifetimes. A critical requirement of building materials used in exterior products is good durability with minimal maintenance, properties that PVC generally provides. Surface coating or chemical treatment is commonly used to protect wood products from the effects of solar UV radiation and moisture, while plastics used in exterior products are generally compounded with UV stabilisers. Efficient UV stabilisers such as hindered-amine light stabilisers (HALS) mixed in with the plastic at only 0.1 to 0.5 wt. % is enough to protect the plastic against premature damage by solar UV radiation under present exposure conditions.

In addition to building construction applications, plastic and wood are also used in other outdoor products, such as in transportation equipment, outdoor furniture, and agricultural equipment. Wood, for instance, dominates the outdoor furniture market. Glass-reinforced polyester (GRP) composite is a common material of choice for constructing small fishing vessels, while increasing amounts of plastics are used in constructing automotive, aircraft, and ocean-going vessels. Plastics are also used in critical alternative energy applications such as in photovoltaic (PV) modules and as coatings in the preservation of cultural artifacts. In all these uses, solar UV radiation is the key environmental agent responsible for compromising performance and determining useful lifetimes of products.

Solar UV-B radiation causes yellowing, chalking, loss in surface gloss, increase in hydrophilicity (capacity to absorb water), and loss in mechanical properties of exposed

materials. Correspondingly, it is predominantly the levels of UV-B radiation in the solar spectrum that is affected by changes in the ozone layer (see Chapter 1). Ozone-related increases in UV radiation levels will therefore tend to accelerate degradation processes in materials, sometimes leading to their premature failure.

An increase in ambient temperatures due to climate change will further exacerbate any light-induced degradation as the UV-induced damage tends to increase with increasing temperatures. Climate change is predicted to result in an increase in temperatures of 1.8 to 4.0°C by 2100, depending on the scenario adopted. The interactive effects of solar UV radiation and climate change on material damage and their mitigation strategies are shown in **Fig. 1**.

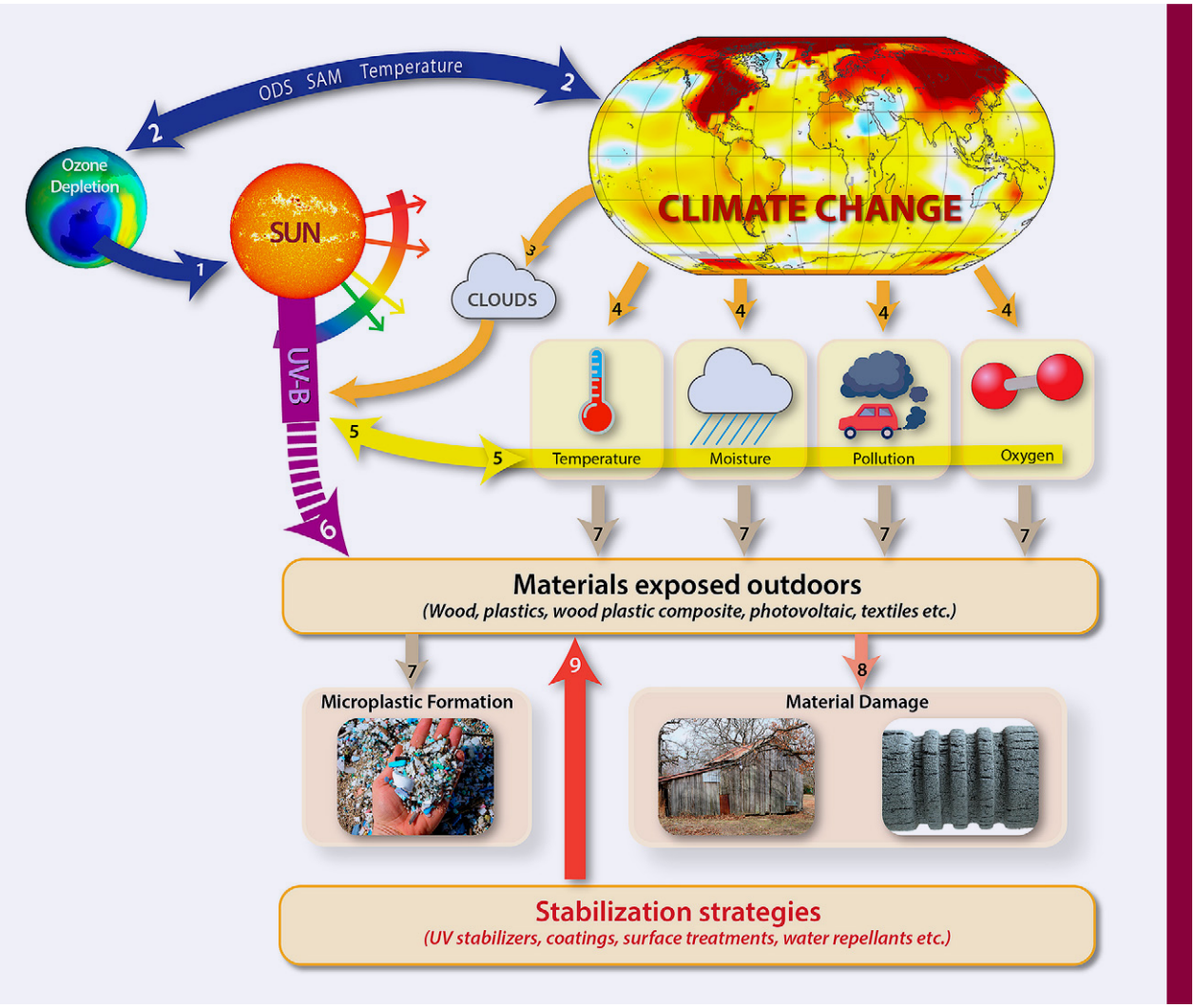

Fig. 1 **Conceptual diagram of the direct effects of stratospheric ozone depletion (1) and interactions with climate change (2, 3, 4, 5) on the amount of solar UV radiation that reaches the Earth. Solar UV radiation and other climatic factors damage materials exposed outdoors (6, 7). This adversely affects service life of materials. UV degradation of plastics generates micro and nanoplastics through fragmentation (7) and often results in discolouration, cracking, chalking, mechanical and chemical degradation (8). Also shown are the methods to stabilise materials against UV radiation and climate change-induced degradation (9).**

While conventional proven technologies are available to maintain the service lifetime of exterior products despite these potential changes in the solar UV radiation spectrum and effects of climate change, this protection is only achieved at a significant increase in the lifetime cost of the products. Newer technologies such as nanoparticle-filled clear coatings for wood and polymeric non-leaching UV stabilisers for plastics are being studied and appear to be particularly promising, but their associated lifetime costs are not known yet.

Weathering of plastic products exposed outdoors over extended periods of time results in their cracking and fragmentation into small pieces. This is most likely with urban litter where plastic products such as films, drinking straws, cigarette filters, cutlery and cups are carelessly discarded after use. Some of these fragments are < 5 mm in size and popularly called micro-plastics (MP). Even smaller sized nanoplastics are produced during degradation. Transport of these MPs into aquatic environments pose a threat to marine biota and is also reported to be found in seafood.

A significant fraction of plastic resins is used in manufacturing synthetic textile fabric. Textiles provide a convenient means of limiting personal exposure to solar UV radiation, thus reducing adverse health effects from such exposure. Textiles can be modified to effectively absorb most of the UV radiation impinging on clothing. Similarly, plastic eye-ware can protect against ocular exposure of individuals to solar UV radiation (see Chapter 2). Plastic films that block or reflect UV radiation are available for use on window glazing to protect the occupants as well as materials used inside buildings (such as carpeting and furniture) from exposure to UV radiation[123].

The relevant research during the past four years that has a bearing on the potential effects of UV radiation, particularly the UV-B component, and the ambient temperature on the lifetime of materials is assessed here.

2 Materials in building construction

2.1 Wood products

Wood is the most commonly-used building material in supporting structures ranging from thatched dwellings in the developing world to large wood-framed constructions in Europe and North America. An environmentally sustainable product with excellent thermal and acoustic properties, wood is ideally suited for use in residential building. Wood is also often available close to the construction site, and moreover, it is cost-effective, carbon neutral, and less energy intensive to produce compared to plastics or metal. Engineered wood products may incorporate fungicides and UV stabilisers that can extend their natural service life.

2.2 Plastic products

Plastics products are used in a wide range of building materials.[2] The major uses of plastic components in buildings are summarised in **Table 1**; this underlines the importance of PVC in this market segment.

Table 1 **Plastics used in building applications**

Component	Plastic material[a]	Traditional material
Siding or cladding	Rigid PVC	Wood, aluminum
Window and door frames	Rigid PVC	Wood, aluminum
Electrical wire coatings & conduits	PVC, PE, rubber, nylon	Rubber, Bakelite
Glazing	PC, PMMA, GRP	Sheet glass
Piping (water & waste water)	Rigid PVC, CPVC, PE, PB	Lead, copper, cement
Decking, fencing & railing	WPC, rigid PVC	Wood
Roofing	PVC, CPE, EPDM, CR	Asphalt, bitumen
Flooring	PVC	Wood, cement

[a] PVC, poly(vinyl chloride); PE, polyethylene; PC, polycarbonate; PMMA, poly (methyl methacrylate); GRP, glass fibre reinforced polyester resin; CPVC, chlorinated PVC; PB, polybutene; CPE, chlorinated polyethylene; EPDM, (ethylene propylene diene) monomer rubber; CR, chloroprene rubber; WPC, wood-plastic composites

The items listed in **Table 1** are those typically used in the exterior of buildings; others such as insulation, water and sewage pipes, building wrap or vapour barriers made of plastics, are not included. In terms of volume use, especially in cladding/siding, rigid PVC dominates the applications sector.[84]

The main advantages of using plastics, especially PVC, in conventional building products are that these are lighter, versatile, easily molded into complex shapes and often have lower cost when compared to alternatives such as wood or metal. However, concerns about environmental sustainability of PVC, the plastic mostly used in building, argue against its continued widespread use. Nevertheless, the double-digit growth rate in GDP in China and India and resulting investment in infrastructure development, has resulted in a strong continuing demand for PVC globally. The industry has also made some progress in improving the sustainability of the material and the key changes undertaken for the purpose are as follows:

c) Discontinued use of mercury catalysts: Mercury-based catalysts have been used historically in manufacturing vinyl chloride monomer, the key intermediate in PVC synthesis. Manufacturers from 128 countries signed the binding Minamata Convention that bans the use of this toxic volatile catalyst from 2017 onwards.[158] A gold catalyst has been proposed as an alternative to the mercury-based one.[78]

d) Phasing out of heavy metal stabilisers used in PVC formulations: The use of lead and cadmium salts as thermal stabilisers in PVC has been a concern as a small fraction of these can migrate out, especially from recycled PVC products.[120] Cadmium in PVC has already been phased out in Europe. Lead compounds have recently also been phased out in PVC products in Europe and the USA. Stabilisers based on calcium-zinc and barium-zinc are being used instead.

e) Using more environmentally sustainable plasticisers in soft PVC products: Conventional plasticisers (the phthalates) are toxic, endocrine disruptor chemicals that may be potent at very low doses. Substitutes for phthalate plasticisers are being evaluated for use with PVC.[102, 108] For instance, the efficacy of cardanol-based plasticisers, epoxidised soybean oil, and their mixtures in plasticising PVC and improving its UV radiation stability, are being investigated.[58, 102]

f) Enabling improved building waste management: Difficulty in managing waste or post-use PVC building products and their low rates of recycling are also key disadvantages to using PVC. In theory, PVC plastic is fully recyclable; however, it is difficult to recycle or incinerate because of the emission of toxic hydrochloric acid on thermal degradation. Also, plasticised PVCs may release the stabilisers and plasticisers such as phthalates into the environment during disposal of waste plastic. However, recently, significant progress has been made in recycling the plastic, with a recent European initiative reporting 569,000 tonnes recycled in 2015. Most of the PVC being recycled consists of extruded door or window frames and pipes. However, there is no significant use of recyclates to refabricate the same building product; they are down-cycled into other, less valuable goods. Nevertheless, increased recycling of PVC can improve its environmental sustainability rating.

The environmental advantages of using recycled PVC in place of virgin PVC resin have been assessed using lifecycle analysis (LCA). Using recycled PVC instead of the virgin plastic results in very significant savings in water and energy as well as in global-warming emissions during the manufacture of the resin (**Fig. 2**). Recycled mixed plastic blocks can potentially be put to a myriad of uses: for example, even the use of plastic bricks in low-cost residential building units have been demonstrated in Colombia (**Fig. 3**). However, there can be potential issues of outgassing and release of particles to indoor air as well as flammability that need to be addressed in such applications.

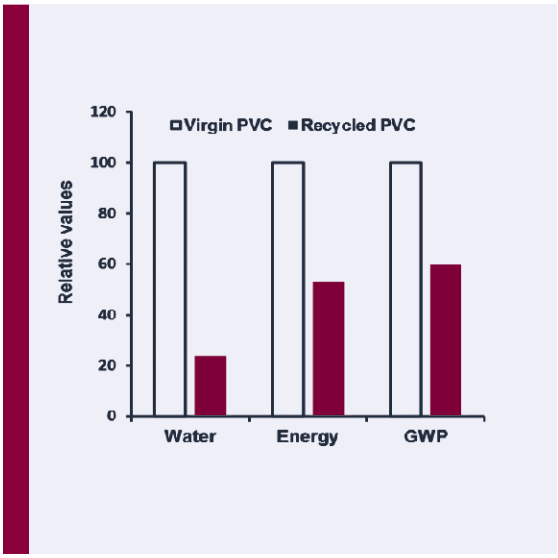

Fig. 2 **The environmental advantages of recycled *vs* virgin PVC for water use, energy demand and global warming potential (GWP) of emissions. The y-axis compares the demand on these resources by recycled PVC and virgin PVC (with the latter set at 100%). The data are for Europe and cannot be directly compared with that for other locations because the Life Cycle Analysis (LCA) methodologies used are different. (Redrawn from data in ref.[179])**

Fig. 3 **Homes constructed with recycled mixed fire-resistant plastics in Colombia. Courtesy of Conceptos Plasticos, Cundinamarca, Colombia.**

3 Solar UV radiation and outdoor lifetime of materials

Plastics and wood undergo degradation under prolonged exposure to solar radiation, resulting in physical, mechanical, and chemical changes on the surface of the material. That UV radiation in the solar spectrum is primarily responsible for initiating the photo-damage of wood, is well established.[70] This was recently confirmed for several additional wood species.[170, 205] The lignin in wood is chromophoric and absorbs UV radiation, initiating degradation (see Chapters 3 and 5); however, no such chromophores are present in common plastics such as polyethylene (PE), polypropylene (PP) and poly(vinyl chloride) (PVC). In these plastics, impurities and products of initial trace oxidation act as chromophores. Outdoor service life of common plastics such as PE,[5] polyester geotextiles[55] and PP[119, 192] is determined primarily by the dose of solar UV radiation and the temperature at which the product is used. In polyolefins (PE and PP), the UV-initiated oxidation is well known to be autocatalytic and a low concentration of chromophoric impurities can initiate significant photodegradation.[48] With wood, the photodegradation is not autocatalytic and the rates vary depending on the species,[166, 178] being primarily influenced by naturally occurring stabilisers.[29] However, with wood[135] and plastics,[188] the rates of weathering and therefore their outdoor lifetimes can be extended significantly by using UV-protective strategies; for example, surface coatings or treatments on wood and the use of UV stabilisers compounded into the bulk of the plastic.

The useful outdoor lifetimes of plastic building products such as siding, window frames, panels and glazing are often determined by photo-damage to the surface, particularly discolouration and chalking, rather than the bulk degradation of the material. While the chemical mechanisms involved are very different from those in plastics, photo-yellowing on weathering of wood is also a surface reaction. Advanced degradation in both classes of materials results in loss of strength leading to cracking of the surface. The damage, however, is often more than aesthetic and can also affect surface integrity (as with chalking of PVC products or surface micro-cracking of PE), or reduction in bulk mechanical properties. Especially in wood, surface cracking facilitates ingress of water into the bulk of the matrix, promoting fungal biodegradation leading to serious deterioration.

3.1 Weathering of polyolefins

The autooxidation reaction sequence that is involved in weathering of polyolefins is very well established. Solar UV radiation initiates the reaction, creating free radicals in the plastic. Propagation of the reaction is via the oxidation of the macro-radical $R\cdot \rightarrow RO_2\cdot$ where R is the polymer molecule) and will continue as long as the plastic and oxygen are available. Hydroperoxides [ROOH] are formed via abstraction of hydrogen by the $RO_2\cdot$ radicals and these, in turn, decompose into radical pairs [RO• and •OH], allowing further initiation, and resulting in autocatalysis. Oxidation reactions of polyolefins that occur in weathering are generally accompanied by a) changes in surface chemistry, b) increases in bulk crystallinity in the surface layers, and c) reduced average molecular weight. Crosslinking and chain scission occur concurrently but, because only the soluble fraction resulting from chain scission is investigated by gel permeation chromatography (GPC), UV-degraded samples yield a lower average molecular weight. The oxidation mechanism and these changes are shown in **Fig. 4**. Spectral changes may indicate an increase in $CH_2 = CR_2$ and $-CH_2 = CHR$ functionalities, indicating chain scission and cross linking, respectively. Degradation is

generally characterised by yellowing of the surface, increase in the carbonyl index, and increased crystallinity of the polymer.

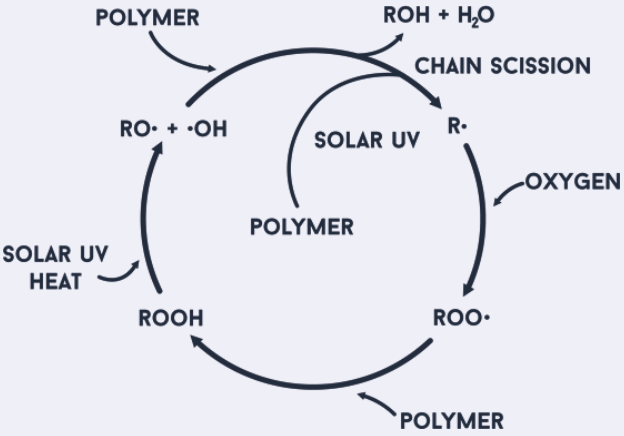

Fig. 4 **Autocatalytic oxidation cycle and the main changes accompanying UV-induced degradation of polyolefins.**

Weathering degradation of the most-used plastic, low-density polyethylene (LDPE), results in the formation of diverse carbonyl compounds on the surface layers of the material.[1] While a recent spectroscopic study unexpectedly showed aldehyde to be the predominant functionality,[192] this is likely a product of early oxidation; ketone and carboxyl functionalities are the main products of oxidation. Addition of transition metal salts to the plastic catalyses the oxidation reactions and is used as a strategy to design environmentally degradable plastics. Cobalt and iron stearates in linear low density polyethylene (LLDPE), for instance, act as pro-oxidants to rapidly reduce the average molecular weight of the plastic, especially at higher intensities of UV radiation.[77] However, even at this high level of oxidation, the average molecular weight of the polymer had not reduced sufficiently to obtain significant biodegradation (< ~20% carbon conversion) by the species *Chryseobacterium gleum*.

In a multi-site outdoor exposure study of PP, both the increase in carbonyl index and development of surface yellowing were quantified.[113] Despite the lack of a firm theoretical basis to anticipate such a relationship, the changes in two properties with the duration of weathering were well correlated in the aggregate data.

Some of the common polymers are partially crystalline, where small volumes dispersed in the amorphous bulk of the polymer are ordered into crystal-like domains. While not true crystals in the conventional sense, these also display melting transitions and act to reinforce the plastic. This morphology invariably depends on thermal- and strain-history of the plastic and is quantified in terms of percentage crystallinity of the material. Because of preferential oxidative degradation of the amorphous fraction as well as chemo-crystallisation, crystallinity of polyolefins generally increases on weathering.[117, 190] Chemo-crystallisation is due to the migration of short polymer chains formed in chain scission leading to their alignment into new crystallites.[73, 113] Competing with chemo-crystallisation is the generation of low molecular weight reaction products and impurities that interfere with crystallisation.[190] In the outdoor weathering of PP, for instance, crystallinity increases in early degradation but decreases thereafter.[114]

A comparison of microstructural changes during accelerated weathering of extruded and laminated samples of PP shows selective degradation of the amorphous polymer.[117] Extruded tapes, because of internal stresses created during processing, underwent faster weathering compared to laminates. Increases in crystallinity of LDPE in outdoor weathering (at a Saharan site in Algeria) confirms the increase in crystallinity of the polymer obtained in accelerated weathering.[73] During 8 months of outdoor exposure, the percentage crystallinity as measured by X-ray diffraction increased, from 36 to 42%. This increased level of crystallinity, along with possible concurrent surface crosslinking, is likely responsible for the observed

increase in tensile strength of PE pipes exposed outdoors.[75] These changes in bulk properties are consistent with the changes in crystallite composition and suggest non-linear change in activation energy with the duration of weathering for the plastic.

3.2 Weathering of wood

Like plastics, wood is susceptible to UV-mediated environmental degradation when exposed outdoors. The cell wall polymers (cellulose, hemicellulose, and lignin) and the low molecular weight extractives in the wood are all readily degraded by weathering. Solar UV radiation is the primary cause of the degradation of wood exposed outdoors.[70, 170, 205] Among wood polymers, lignin is a strong absorber of solar UV radiation due to the presence of many chromophoric groups in its chemical structure and hence is the most affected component by UV radiation.[18, 19, 170] Weathering decreases the mechanical integrity and the aesthetics of wood products.[110] The rate of degradation is often measured by the degree of surface discolouration, which is a critical property for sawn-wood products. The hydrophilicity of the UV-degraded surface of wood increases and facilitates biotic degradation by fungal action, limiting their service lifetimes outdoors.[27]

Surface colour change from exposure of wood to UV radiation decreases with increasing wavelength of radiation as recently demonstrated for Asian white birch wood veneers.[110] The wavelength dependence of the photodamage is described by a wavelength sensitivity spectrum in the form of an action spectrum. A novel laboratory methodology to conveniently derive action spectra for materials exposed to UV-visible radiation has been recently developed.[68] Improved methodology allows simultaneous exposure of different parts of a single sample to different monochromatic wavelengths resolved with a xenon light dispersed using a diffraction grating. While the principle has been used previously, for instance in the Okazaki Large Spectrograph facility in Japan, its adaptation into a desktop instrument is a key innovation. The method was used to study photo-yellowing of mechanical pulp where newsprint samples were exposed to resolved xenon source radiation in the wavelength range of 250–500 nm.[68] Information on wavelength-sensitivity does not include potential synergistic (or compensatory) effects at different wavelengths in the full solar spectrum. Activation spectra of degradation generated for solar radiation includes such interactions and considers the entire distribution of spectral irradiance of sunlight.

The main consequences of degradation of lignin in wood are the rapid discolouration and loss in mechanical properties.[205] Changes in surface chemistry are detectable by ATR-FTIR spectroscopy[26] and indicate progressive loss of lignin with the duration of exposure.[110, 166, 169, 205] Weathering is generally localised to a surface layer of the wood[81, 90, 205] and is rapid enough to yield visible discolouration within the first few hours of laboratory exposure to a xenon source. In natural weathering of softwood (spruce and larch) and hardwood (beech and oak), most of the lignin on the surface is degraded after only 2 months of laboratory exposure to simulated solar (xenon source) radiation. In bamboo wood, the maximum colour change was observed within 3 months of natural weathering and was accompanied by the degradation of lignin and an increase in crystallinity of the cellulose fraction of wood, as determined by FTIR spectroscopy.[90] The photo-oxidation of lignin results primarily in the formation of (water soluble) carbonyl derivatives resulting in yellowing of the wood surface.[18, 30, 198] Spectral signatures of common oxidation products of lignin are generally detected on UV-exposed wood surfaces.[166, 205] It is the formation of singlet oxygen, a particularly reactive

26 Attenuated total reflectance-Fourier transform infrared spectroscopy.

radical species, that facilitates the degradation reactions of lignin and results in formation of carbonyl moieties in weathered wood.[30] This, in turn, increases surface wettability, making the carbohydrate-rich degraded wood more susceptible to biological decay.[27]

Along with lignin, some cellulose is also degraded by solar UV radiation, although at a relatively slower rate; however, it is the amorphous cellulose fraction that is preferentially degraded.[36, 90] The relative inertness of crystalline cellulose to degradation by UV radiation was confirmed for spruce wood,[36] bamboo[90] as well as wood-plastic composites[66] in recent studies. The surface layer of wood, therefore, becomes progressively richer in crystalline cellulose as weathering continues.[36, 62] The cellulose-rich surface serves a UV-protective function limiting further degradation as shown for several types of wood.[180] This suggests that preliminary pre-degradation with UV radiation may help stabilise wood against discolouration,[180] but the relevant process conditions for large-scale use and economic feasibility have not yet been established.

The L* (lightness), a* (greenness-redness) and b* (yellowness) coordinates uniquely specify single hues in the CIE Lab colour space, allowing any colour change to be quantified. Surface discolouration of wood typically results in a decrease in L* and increase in b* indices.[36, 205] Yellowing rates for a variety of wood species exposed to solar UV radiation have been reported in the literature including several recently-studied wood species.[19, 36, 156] The change in the ratio of lignin/carbohydrate (as reflected in the spectral intensity ratio [I_{1507}/I_{1377}]) with the duration of exposure, revealed a loss of 50% of the lignin content in chestnut wood within 48-h of accelerated laboratory exposure.[19] These changes are far more pronounced during initial stages of exposure[19, 166, 205] and are confined in a thin surface layer of wood.[81, 90, 205] A study on depth profiling of photodegraded sugi wood (*Cryptomeria japonica* D. Don) by confocal Raman microscopy indicated a degradation zone up to about 500 μm in depth.[81] The rates of these changes are species-dependent but the largest changes occur within the first few hours (even within 6 h),[166] and the maximum effect is reached after 24 h of laboratory exposure with different varieties of wood.[18, 19, 23, 25, 166]

The colour changes correspond to lignin degradation and the formation of carbonyl groups produced during photo-degradation of several softwood[166] and hardwood species.[19, 23, 110, 166] A similar correspondence was also reported between the residual lignin content assessed by FTIR and the change in tensile strength during natural weathering of fir-wood.[205] If generally applicable, such correlations may allow the simpler, non-invasive measurements (particularly yellowness index), to be used as a proxy for oxidative changes and loss in mechanical properties of weathered wood. Development of non-invasive methods to monitor surface photodegradation is important for predicting service life and developing protective coatings for wood.[18, 25]

The chemical degradation of wood by UV radiation results in the destruction of cell wall structure. Development of radial micro-cracks in cell walls, complete deterioration and thinning of the cell walls in young parenchyma tissue (non-vascular, ground tissue), and degradation of pit membranes in vessels as well as in parenchyma cells are generally observed.[135, 148] The presence of spores and dust particles further affect the structure of wood under natural weathering conditions.[180] Anatomical changes in the top surfaces of Cumaru wood (*Dipteryx odorata* (Aubl.) Wild.) after natural (36 months) or artificial (12 weeks) weathering are compared to that before weathering, in **Fig. 5**.[148]

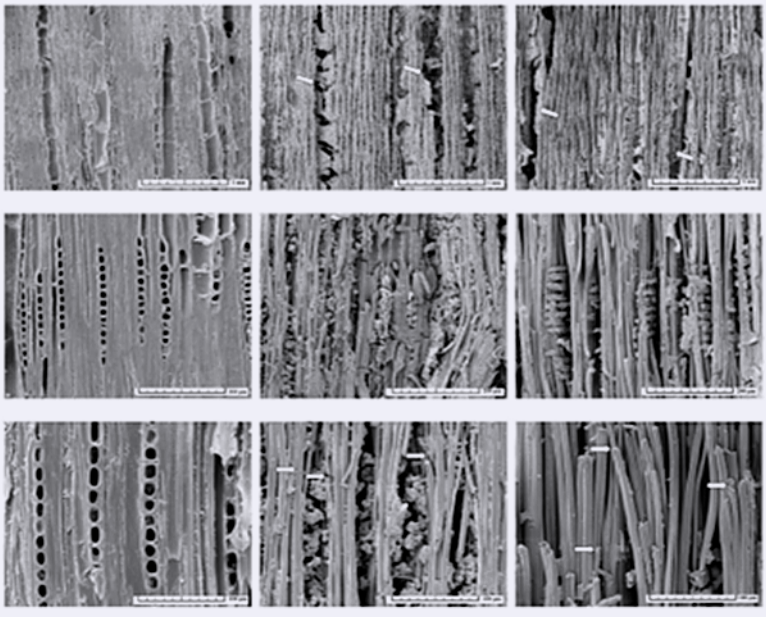

Fig. 5 **Anatomical changes in the top surfaces of Cumaru wood (*Dipteryx odorata* (Aubl.) Wild.) after natural (36 months) and artificial (12 weeks) weathering. 1st row magnification 100-X; 2nd row magnification 500-X; and 3rd row magnification 1000-X (reproduced with permission from ref.[148]). Xenotest weatherometer employs a filtered xenon source to provide UV-visible radiation with a spectral distribution that closely matches solar radiation. Reference image is for sample prior to weathering.**

3.3 Wood-plastics composite material

Composites of wood and plastics (WPC) are popularly used in outdoor building applications, accounting for about 50% of the volume of outdoor structures, especially in construction of fences and decks in the USA. The fastest growing application, however, is in automobile interiors. While the annual global production of WPC is small (4.26 MMT in 2016), the market sector is projected to grow at 12.3% annually until 2022.[204] WPC typically use PE, PP and PVC and may include both virgin and post-consumer recycled resin.[69] In applications for automobile interiors and outdoor use, the material is routinely exposed to solar UV radiation and as would be expected, the success of WPC as an outdoor building material is invariably related to its stability under exposure to solar UV radiation.[33, 50, 66, 193] Degradation of WPCs by weathering generally depends on the UV wavelength, intensity, and exposure time.[115]

As with wood, exposure of WPC to solar radiation results in surface colour change,[146, 174] increased carbonyl concentrations and loss in mechanical properties.[42, 122, 146, 162] The mechanism of WPC degradation under solar radiation can be understood in terms of chemical features observed in the degradation of the wood and plastic components in the composite by UV radiation. Weathering of PP-based WPC results in visual as well as microscopic changes on the surface, cracking and weight loss over 90–180 days outdoors, and damage from pulled-out wood fibres at the surface.[193] A recent study shows that micro-crack development

and surface bleaching[31] are also important degradation mechanisms of WPCs. Generally, their mechanical strength decreases in parallel with these visual changes[162] and the sites of surface defects are typically the protrusions of wood fibres. These changes are consistent with those anticipated by the present understanding of photodegradation of wood.

Given the limited product range of extruded WPCs available commercially, the appropriate metrics to be used to assess their weathering are not clear. Tensile tests,[50] flexural tests[11] and microscopic quantification of cracks[193] have been used for this purpose. A recent meta-analysis of 44 datasets on WPC found that Young's modulus and modulus at break were the best parameters to assess their weatherability.[50] Exposure to solar UV radiation was found to increase rates of biodegradation (as measured by respirometry) in composites of polypropylene (ethylene vinyl acetate) copolymer (PP/EVA;70:30 w/w) with wood-flour.[27] In PP-wood fibre composites, the loss in mass during subsequent biodegradation was > 300% higher for material weathered outdoors for 90 days than for the control (reference material). A similar finding has been reported for degradation of rice straw.[105] As the wood fraction is likely to undergo faster UV-degradation relative to the plastic and is relatively more hydrophilic, this is an expected result for WPCs, based on established observations of photodamage facilitating biodegradation of wood (see Chapter 5). As oxidation of the plastic fraction does not facilitate significant biodegradation on weathering of WPC, oxidation of the wood fraction is responsible for the increased biodegradation.

4 Effects of temperature on the weathering of plastics and wood

As degradation reactions are generally accelerated at higher temperatures, any increase in ambient temperatures due to climate change will aggravate the damaging effects of UV radiation on materials. The temperature-dependence of degradation reactions is described by the well-established Arrhenius equation that is used to estimate the increased rates of degradation obtained at higher temperatures.[13, 145]

In outdoor exposure of materials, the dose of solar radiation is usually the key determinant of the rate of photo-oxidative degradation,[167] for instance, as shown with PE[5, 192] and PP[119] in recent studies. However, recent comparative outdoor weathering exposures of PP at multiple locations, found temperature to be the dominant variable that determined the rates of degradation.[113, 190] Where the variation in solar radiation dose between sites is small, the differences in the temperature can determine the relative rates of weathering.

In indoor exposures, materials are not exposed to direct solar UV radiation. Under these conditions, diffuse UV radiation, ambient temperature, and air pollutants are the principal agents of weathering. In a weathering study on 18 types of plastics, where direct sunlight and precipitation were excluded, the rate of yellowing discolouration was determined primarily by the dose of diffuse light (including scattered UV radiation) rather than the temperature.[138] These conditions pertain to weathering of books and documents as well as art and cultural heritage items stored indoors in museums and libraries where only diffuse solar radiation is present. The study also found that NO_x (from traffic exhaust), not generally included as a parameter, was a significant agent of yellowing discolouration of material. Depending on the exposure conditions, temperature, diffuse light, or even humidity can be the dominant determinant of the rate of outdoor weathering.

As degradation reactions of materials are oxidative, the concentration of available oxygen will also affect the rate of the process. A novel form of the Arrhenius equation that also includes the oxygen partial pressure as a variable has been proposed for weathering of PP[114] (Eq. 1).

$$Ln\ k = p\ Ln\ (I) + qLn\ (o) - (\Delta E/RT) \quad [1]$$

where k is the rate constant, (O) is the partial pressure of oxygen, ΔE is the activation energy, T is the absolute temperature and R is the gas constant ($Jmol^{-1}K^{-1}$). The usefulness of this extended form of the equation for modelling the weathering process in common plastics requires further verification. For exposures at high-altitude locations this new equation [1] might be useful.

The findings for wood generally parallel those for plastics, and the extent of degradation, especially surface yellowing is also accelerated at higher temperature.[62, 161, 170] However, interpreting data on light-induced discolouration of wood is complicated by the different components of wood (cellulose, hemicellulose, lignin, and extractives) undergoing weathering independently, and at different rates, on exposure to solar UV radiation. With wood products, such as those of Norway spruce and beech, humidity can also determine the service lifetimes because of biodegradation subsequent to surface photo-damage.[170] Discolouration of these wood species after only 20–60 h of outdoor solar radiation can be ~17% higher at 100°C compared to 30°C.[170] The rate of photodegradation of hardwood (beech, *Fagus sylvatica* L.) and softwoods (Scots pine and spruce) depends on ambient temperature, with softwood species being relatively more sensitive to exposure to UV radiation at elevated temperatures.[178] This is attributable to the relatively higher lignin fractions in softwoods and the higher photo-susceptibility of the lignin.

5 Stabilisation of materials against weathering

With the predicted recovery of the stratospheric ozone layer, solar UV radiation received at the Earth's surface is not expected to increase in the future (see Chapter 1). However, the intensity of UV-B and UV-A radiation can still increase locally because of climatic factors such as clearer skies in the tropics that may also experience high ambient temperatures. Available and emerging stabiliser technologies are expected to maintain the service lifetimes of wood unchanged under such exposures.[26] These are based on covering the surface with a UV-opaque layer, using a UV-absorbing additive in the material, or using stabiliser that interferes with the basic oxidation reactions as shown in **Fig. 4**. Stabilisation and insights on stabilisation mechanisms for wood material are assessed under three broad categories.

a) Surface treatment and modifications

b) Thermal modification

c) Use of nanoscale fillers in surface coatings

5.1 Surface treatments and modification of wood

Surface treatment is a cost-effective means for solar UV stabilisation of wood.[87] Conventional approaches such as copper-treatment, acetylation, and reaction with epoxidising reagents have been reported for this purpose.[199] Copper ethanolamine or copper azole, for instance,

is well known to impart both UV stability and fungicidal activity to Japanese Larchwood.[74] Copper ethanolamine reacts with the -OH groups in lignin, converting them to carboxylates, retarding the degradation of lignins by UV radiation. However, sustainability concerns regarding leaching of copper compounds out of the wood may limit its continuing use in the future.[72]

Acetylation of wood provides multiple functionalities, such as increasing resistance to fungal decay, dimensional stability, and resistance to UV radiation.[136, 152] However, use of the conventional anhydride reagents to acetylate wood yields acid byproducts that may damage the material. The acetylating agent, isopropenyl acetate, avoids this disadvantage and stabilises wood against UV-induced degradation while also enhancing its hydrophobicity and resistance to fungal attack.[56, 57, 125] Acetylated wood underwent bleaching as opposed to yellowing on exposure to simulated solar UV radiation in the laboratory. Alternatively, treating beech wood with thermosetting N-methylol melamine and phenol-formaldehyde resin also improved its weathering performance.[87] The treated wood coated with an acrylic coating showed improved UV-stability compared to acrylic-coated and uncoated controls. Despite the effectiveness of the chemical modification in stabilising wood against solar UV radiation, the cost-effectiveness of the process in high-volume use needs to be improved to encourage its high-volume use.

Organic surface coatings or paints that screen out solar UV radiation can also be an effective approach to stabilising wood. Epoxidised soybean oil effectively protected the surfaces of silver fir (*Abies alba* L) wood against photooxidation under solar UV radiation.[151] With Scots pine wood (*Pinus sylvestris* L.), treating the surface with 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone or an epoxy functionalised soybean oil also effectively enhanced UV-protection of clear-coated wood under both accelerated (up to 4,000 h under xenon radiation) and natural exposure outdoors (up to 14 months).[133] However, using epoxidised linseed oil was ineffective in arresting discolouration and delignification of Scots pine wood.[76] The reason for this disparity is not clear and the organic surface coating may have to be matched with different varieties of wood for effective stabilisation. The process is again not cost-effective for high-volume use.

Paints containing inorganic pigment or organic UV-stabiliser compounds can shield the wood from exposure to UV radiation. Conventional light stabilisers typically used in plastics, such as UV absorbers and hindered amine light stabilisers (HALS), compounded into paints and varnishes used on wood, are effective in controlling discolouration and mechanical damage of both softwood and bright hardwood.[47] However, these stabilisers do not prevent bleaching of dark woods (rosewood, ebony, mahogany, or black walnut) or heat-treated wood exposed to UV radiation.[137] There is a need to develop alternatives for use with this class of wood. Most of the recent work is on using nanoscale fillers in wood coatings to obtain efficient protection from UV radiation (see section 5.3 below).

5.2 Thermal modification of wood

Heating wood (at 180–240˚C) in the absence of air is an environmentally sustainable means of improving properties of wood for outdoor applications. The treatment yields a stable hydrophobic surface with improved resistance to decay.[24] The success of the treatment depends on the species of wood and the temperatures employed. The process is effective in controlling discolouration of certain hard- and soft-wood species exposed to UV radiation as summarised in **Table 2**.

The presence of chemically different extractives in different wood species may perhaps explain the unexpected variability of results shown in **Table 2**.[137, 160] Different extractives can act as UV stabilisers or themselves photooxidise into coloured products at different rates. There is insufficient information available to predict how a given variety of wood will respond under UV irradiation after thermal treatment. Furthermore, the treatment conditions, temperature and duration, can be key variables that determine the result. However, heat treatment can be a cost-effective and environmentally sustainable treatment that deserves further investigation.

Table 2 **Effectiveness of thermal treatment on different species of wood against weathering.**

Type of weathering (species of wood)	Property tested[a]	Effectiveness against photo-degradation	Reference
Accelerated weathering (Turkey oak wood)	Colour changes, FTIR, SEM	Yes	Ref.[168]
Natural Weathering (Ash, iroko, Scots pine, spruce wood)	Colour changes, Mechanical properties, Surface roughness	Yes	Ref.[171]
Accelerated weathering (Scots pine, Norway spruce)	FTIR spectroscopy, micro-tensile strength testing	Yes	Ref.[6]
Natural weathering (Aspen wood)	Colour changes, FTIR	No	Ref.[34]
Accelerated weathering (Black locust, Poplar)	Colour changes	No	Ref.[169]
Accelerated weathering (Poplar, black locust)	Colour changes	No	Ref.[127]
Accelerated weathering (*Larix* spp.)	Colour changes, SEM, FTIR	No	Ref.[189]
Accelerated weathering – CO_2 laser irradiation (Lime wood)	Colour changes, FTIR	No	Ref.[96]

[a] FTIR, Fourier transform infrared spectroscopy; SEM, scanning electron microscopy

5.3 Nanoscale fillers for UV stabilisation

Theoretically, using nanoscale fillers (< 100 nm), in place of conventional mineral fillers with a larger average particle size, makes good sense as the specific surface area of pigment particles increases exponentially as the particle size is reduced. Fillers that absorb solar UV radiation impinging on them protect the underlying wood or plastic. With a larger specific surface area available to absorb solar UV radiation, a smaller volume fraction of a UV-absorbing nanofiller can economically substitute for a large fraction of a conventional filler. Based on initial test results, at the nanoscale, common metal oxides, especially zinc oxide (ZnO), titanium dioxide (TiO_2), and cerium oxide (CeO_2) appear to be excellent absorbers of UV radiation, as long as these do not catalyse photodegradation. However, some of these metal oxides can indeed act as photocatalysts or pro-oxidants, a property exploited in the design of self-cleaning coatings. Grades of oxides used as stabilisers are usually coated with an inert shell of a material such as silica. A key advantage of inorganic fillers is that, unlike organic UV stabilisers, they do not degrade under exposure to UV radiation.

The efficacy of nanofillers as UV stabilisers, however, appears to vary with the specific plastic-filler combination in question. They appear to be particularly efficient in some combinations as shown in **Table 3**.[46, 140] However, in other plastics, the nanofillers unexpectedly accelerate photodegradation, as measured by changes in carbonyl index, chemiluminescence, and crystallinity of the plastic. The relative efficacy of two competing mechanisms, i.e., light-shielding by the nanofiller and their potential pro-oxidant characteristics, yields the net stabilisation effect observed. Further studies into their mechanisms of action in the specific plastics of interest will be needed prior to broader application of nanofillers as stabilisers in plastics. Another important drawback to their full exploitation is the difficulty in obtaining good dispersions of the nanofillers in plastics.[38] Some of the disparity in the performance of nanofillers as UV stabilisers of plastics may be a result of poor dispersion of nanofiller in the plastic matrix.

Table 3 **Effectiveness of nanofillers in stabilising plastics under laboratory-accelerated weathering conditions.**

Plastic type[a]	Nanofiller concentration (wt%)[a]	Property tested	Effectiveness	Reference
HDPE	Wood powder and ZnO (1–4%)	Tensile strength, colour, carbonyl index	Yes	Ref.[146]
PP	ZnO (1%)	Tensile strength, carbonyl index, and crystallinity	Yes	Ref.[159]
PS	Nanoclay (2%)	Carbonyl index	No	Ref.[38]
PLA	Nanoclay (1%)	Tensile properties	Yes	Ref.[85]
PLA	Rutile TiO_2 (1%)	Tensile properties	Yes	Ref.[191]
PMMA	Rutile TiO_2 (2%)	Weight loss	Yes	Ref.[130]
PP	TiO_2 Nanotube (5–7%)	Chemiluminescence, carbonyl index, and crystallinity	No	Ref.[197]
HDPE	Bamboo fibre and TiO_2	Colour, cracking, and tensile properties	Yes	Ref.[46]

[a] HDPE, high-density polyethylene; PP, polypropylene; PLA, poly(lactic acid); PS, polystyrene; PMMA, polymethyl methacrylate. TiO_2, titanium dioxide; ZnO, zinc oxide.

5.3.1 Nanofillers in wood coatings

Nanofillers can also act as UV stabilisers in wood[66, 131] and in textile fibres.[3] Nanomaterials, including graphene,[181] zirconium dioxide,[182] iron oxide,[52] TiO_2,[184] and CeO_2[112] have successfully been either deposited or synthesised on wood surfaces. In laboratory-accelerated tests, all these formulations effectively controlled UV-induced discolouration of wood. Two approaches are used to treat wood surfaces with nanofillers: a) the nanofiller can be generated *in situ* on the surface layer of wood; or b) the filler can be directly deposited on the surface or dispersed in a clear coat.

There is considerable research interest on *in situ* generation of inorganic nanoparticles on wood. For instance, with spruce wood, ZnO nanoplates were generated *in-situ* using

a precursor absorbed into the wood surface. The treated spruce wood showed > 75% less discolouration compared to untreated wood in laboratory accelerated weathering with simulated solar (xenon source) radiation for 102 h.[61] Arrays of ZnO nanorods (typically < 100 nm in length) generated directly on the wood surface by a different process, were similarly effective in reducing the discolouration by 80% compared to untreated Chinese white pine wood exposed to 200 h of simulated solar UV radiation in the laboratory.[93] Despite these impressive successes in the laboratory, *in situ* generation of nanoparticles on wood surfaces is complicated and not cost-effective for commercial use at the present time. Innovative simpler methods of processing, coupled with low-cost reagents, would make this approach practical for volume application.

Presently, the use of fillers in surface coatings is likely to be the more cost-effective approach.[131] Nanoscale oxides that absorb UV radiation can be used at low weight fractions to efficiently shield the wood surface from solar UV radiation. Coatings of wood surfaces with 0.36–0.46 kg m^{-3} of either nano-ZnO or nano-TiO_2,[154] those with 1–3% of either ZnO, TiO_2 or CeO_2,[126, 164] or coating compounded with 1–1.5 wt% of any of these fillers,[124] were all recently investigated for their UV-stabilising effectiveness. All treatments reduced the discolouration of wood species by up to 57% in natural and/or simulated exposure to solar UV radiation. A similar effect was found with nano-ZnO in poplar wood (*Populus tomentosa* Carr.),[39] composites of beach wood-polyethylene[146] and with nanotitania on a bamboo-polyethylene composite.[45] An organic nanofiller that was found to be effective in improving colour stability of wood is crystalline nanocellulose. At only 0.5–2.0 wt%, the nanofiller improved both mechanical integrity as well as colour stability of the wood in laboratory exposures of up to 1,200 h to simulated solar radiation.[177]

5.3.2 Nanofiller as UV-protectants in textile fibres

Nanofillers are used in the textile fibre industry as "nano-finishing" material where nanofiller particles are applied to the fibre surface to impart UV-blocking or other properties, such as biocidal activity. Compared to conventional organic UV stabilisers incorporated into fibres, the nanoparticles are more durable under UV irradiation. Nano-finishing cotton fibres[95] and nylon[150] with ZnO and carbon nanotubes (CNTs) show promise in this regard. For instance, cotton fibres functionalised with ZnO and CNT nanocomposites at a level of ~22% by weight, increased the UV protection factor (UPF) of cotton from 6 to 40.[195] Recent studies on nano-ZnO[200] in polyester or cerium-doped nano-ZnO on cotton fibres[53] confirmed their superior UV-blocking properties. Nanoparticles of TiO_2,[3, 83, 183] graphene,[15] and gold[194] have also been explored for UV stabilisation of fibres. More work is needed to assess the commercial potential of this emerging technology especially because of the high cost of nanofillers used in these initial studies. Furthermore, surface-applied fillers on fabric can be released into the environment during laundering. Releasing nanoparticles into the environment is generally undesirable as their fate and impacts on the ecology are largely unknown.

There is emerging interest in using plant-derived dyes as UV stablisers with some yielding as high as a ≥ 50 protection factor in natural fibres such as cotton.[54] Even where ZnO is used as a UV-protectant, adding an Aloe gel to cap the filler allowed for UPF values of untreated linen fabric to improve from 7 to 61.[202] Treatments used in these laboratory studies need further investigation and development prior to production in commercial processes. The approaches, however, show considerable potential as replacements for synthetic dyes if the natural dyes do not undergo rapid fading, which would then limit the service life of the fabric.

5.3.3 UV-shielding glazing

Glazing in both residential buildings, greenhouses, and vehicles effectively screens solar UV-B and some of the UV-A radiation, protecting people and crops in these enclosures. Nanoparticles such as CeO_2 created *in situ* within the glazing[201] or generated on multilayers on the glass surface,[44, 203] do perform well but these approaches do not appear to be cost-effective at this stage of development. Protective plastic films carrying UV-absorbing nanofillers filter out most of the solar UV radiation, when applied to the surface of glazing.[106, 149] Polypyrrole nanoparticles compounded into poly(acrylic acid) films, for instance, filter out 47% of solar UV radiation when applied as a 0.34 mm film that contains only 0.05 wt.% of the nanoparticles.[32] These films are beginning to be available commercially.

5.3.4 Risk of release of micro- and nano-particles from nanocomposites

An emerging issue with production and uses of nanocomposites is the potential release of nano- or micro-fragments from these products as weathering proceeds.[35, 41, 92] This occurs because the embrittled surface layer of a degraded nanocomposite can release fragments[187] that are micro-sized (2–10 μm), or even individual nanofiller particles, by mild abrasion during handling. For instance, in LDPE food packaging films filled with nanoclay, the filler improves the mechanical properties as well as UV-stability of the product but increases its propensity to release nanoparticles when the weathered material is agitated or sonicated in water.[64] With food-contact products the potential human exposure of consumers to these fragments is a particular concern. As some nanofillers such as ZnO[67] and carbon nanotubes[157] are potentially toxic and may present a risk to humans and the environment, this can be a serious concern.[65, 94] It is critical to select non-toxic nanofillers for composites intended for food-contact applications.

Thermoset polymers such as epoxy composites, especially the glass-reinforced polyesters (GRP), are engineering materials used in outdoor applications. Recent observations on the cyclic exposure of vinyl-ester epoxy-based GRP composites to simulated solar (xenon source) radiation (at 80°C, in a fluorescent UV weathering tester) for a total of 1000 h resulted in the generation of microparticles on the surface of the composite.[111]

Carbon nanotubes are used as a reinforcing nanofiller in common plastics to increase their stiffness and strength[104] and to increase their electrical conductivity.[4] With CNT-containing nanocomposites, however, photodegradation results in the surface layer being oxidised, leaving behind a concentrated consolidated mat of CNT on the surface.[65, 100, 129] This mat of entangled CNT is held together by Van der Waals forces and is an efficient light absorber, protecting the underlying plastic matrix. Consequently, the release of nanoparticles into the environment even after prolonged exposure is retarded. In a study on CNT-reinforced with epoxy, the surface layer mat of CNT obtained was 2.5 microns thick and the release of micro- and nanoparticles decreased with duration of weathering.[157] However, these observations are based on initial laboratory studies on selected nanocomposites and needs further validation. For example, the integrity of the surface mat of CNT formed on the embrittled surface layer exposed to elements, particularly rain, may still result in release of micro- and nano-particles.

5.4 Naturally-derived UV stabilisers

The plastic and wood industries continually strive to improve their UV-stabilisation technology to further extend the service lifetimes of materials used outdoors. However, these improvements must also explore sustainable choices consistent with worldwide public interest in improving environmental defensible plastic materials. A particular outcome of this trend is reflected in the general preference for stabilisers that are not only effective but are also environmentally sustainable. Most UV stabilisers used today are toxic[118] and can migrate from bulk to the material surface and then be released to the environment.[98] With several legacy additives such as lead compounds used with plastics being phased out because of their adverse environmental impact, the search for better technology is receiving focused attention.

5.4.1 Wood-derived lignin as UV stabilisers for plastics

In the search for environmentally sustainable natural stabilisers, the wood-derived stabilisers are receiving attention. Lignin constitutes about 16–25 wt% of hardwood and 23–35% of softwood and is a natural, complex amorphous organic polymer. Native lignin has a highly-branched structure consisting mainly of p-coumaryl, coniferyl, and sinapyl phenolic moieties (**Fig. 6**) and can be readily extracted with solvents such as dioxane or via acid digestion. Depending on how it is extracted, different grades of soluble lignins (such as Kraft lignin, milled-wood lignin and alkali lignin) are obtained. These grades may differ somewhat structurally, but all of these are generally rich in substituted phenols.

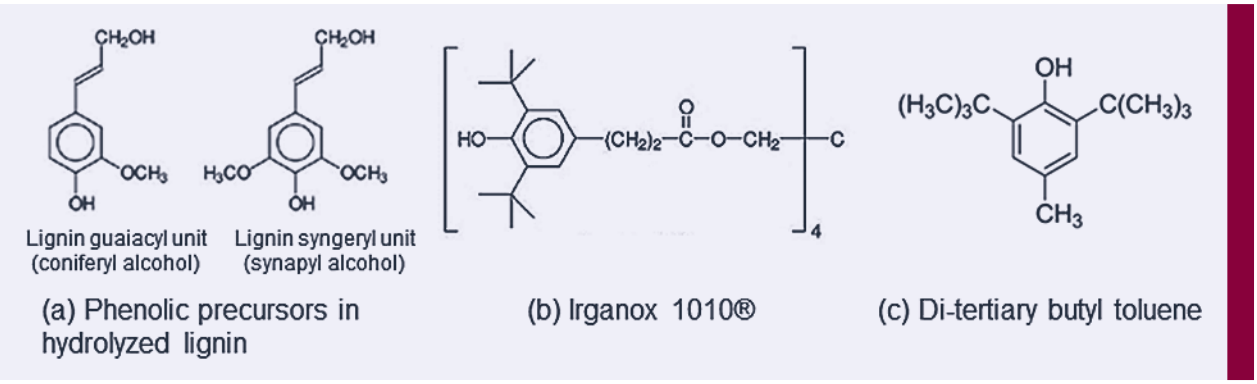

Fig. 6 **Chemical structures of phenolic precursors in hydrolysed lignin (a), and the hindered-amine stabilisers, Irganox 1010 (b), and di-tertiary butyl toluene (c).**

Synthetic hindered phenols are well-established as effective commercial UV stabilisers for use in polyolefins, where they act via radical scavenging. The structural similarities between the two groups of compounds are apparent (**Fig. 6**) and the phenolic functionalities in lignin also make it a good UV and oxidation stabiliser.

Powdered wood itself contains enough lignin to impart UV-stability to plastics.[108] Lignin filler is generally known to act as a UV stabiliser in PP.[51] While the modulus of elasticity of PP composites filled with wood powder was reduced by *ca* 30% when exposed to laboratory-accelerated weathering for 960 h, no such decrease (instead even a slight increase) was obtained with lignin-filled PP under the same exposure conditions.[51] However, powdered wood fillers in plastics potentially introduce weather-related damage at the sites of

protrusion of individual wood fibres at the surface. Compared to powdered wood, native lignin and extracted lignin are superior stabilisers in PP.[139] At 2 wt%, in the plastic, extracted lignin was found to be a very good radical scavenger in PP, stabilising the plastic against solar UV radiation over 2000 h of laboratory exposure.[31] At comparable concentrations, Kraft lignin extracted from *Eucalyptus sp.* performed even better than a conventional hindered-amine light stabiliser as the primary UV stabiliser in PP.[51] This study involved simulated solar UV exposure with a xenon source and assessed degradation in terms of changes in the Young's modulus of the plastic. While the economics of their high-volume use as stabilisers are not available, this bio-derived, environmentally sustainable class of UV stabilisers for commodity plastics shows promise.

Depolymerised lignin is a mixture of its constituent substituted phenols that has at least the same stabiliser effectiveness as native lignin when used as a stabiliser in PE and PP.[79] Lower molecular weights of these phenolics allow for better solubility and dispersion in the plastic matrix. PP exposed to simulated solar UV radiation could be stabilised against loss in stiffness by depolymerised lignin. A 2.5 wt%, depolymerised kraft lignin was as effective as 0.5 wt% of a conventional stabiliser when tested over a duration of 200 h of accelerated laboratory exposure. Similarly, the addition of these lignins to biodegradable poly(lactic acid) (PLA) increased its impact strength as well as resistance to UV-induced photodegradation under accelerated laboratory exposure.[163]

In wood, where 16–35% of the bulk is lignin, it is the main chromophore that absorbs solar UV radiation and initiates photo-oxidative degradation. However, the 1–2 wt% of lignin used as a stabiliser in plastics does not significantly increase the absorption of solar UV radiation by the composite but provides a high enough concentration of phenolic functionalities to ensure exceptional stabiliser activity. The use of derivatives of lignin such as butylated lignin as UV stabilisers in plastics also show particular promise.[196] While likely to be a cost-effective practical technology, the lignin-derived stabilisers must evolve into well-defined standardised additives to be able to compete with synthetic alternatives.

5.4.2 Wood extractives as UV stabilisers for wood

Extractives are compounds that give wood its colour; they constitute generally ~1–5 wt% of the wood and are typically mixtures of terpenes, terpenoids, simple phenolics, polyphenols, and aliphatic compounds. Some of these compounds can act as radical scavengers and therefore as UV stabilisers for plastics [21, 118] and wood.[29, 30]

The catechol flavonoids in *Acacia confusa* wood-extractives, for instance, function via multiple mechanisms to photostabilise several wood species against discolouration and degradation of lignin on exposure of the wood to simulated solar radiation.[30] In laboratory exposures, extractives were as effective as synthetic UV stabilisers in controlling discolouration of wood exposed to simulated solar radiation. Tannins (proanthocyanidins) extracted from the bark of *Pinus radiata* also show a similar stabilising effect.[59, 60] Incorporating either native or modified tannins at concentrations of < 0.5 wt% in acrylic coatings controlled the discolouration of timber in outdoor weathering studies, again outperforming conventional synthetic UV stabilisers at similar concentrations.[59, 60] Extractive-derived UV stabilisers, along with lignin-derived compounds, show particular promise as potential environmentally-sustainable stabiliser additives in plastics.

6 Useful lifetimes of photovoltaic modules

The global capacity of installed solar photovoltaic (PV) modules is 234 gigawatts and 85% of the panels have been in use for less than 5 years.[121] While they are expected (and often warranted) to perform for a period of at least 25 years, the actual outdoor lifetimes of PV modules cannot be practically assessed for at least another two decades of use. Only laboratory-accelerated weathering tests can be relied upon to predict their service lifetimes and modes of failure. These laboratory tests need to be designed carefully, considering all the stresses encountered by the modules under field conditions and rely on identifying early signs of module failure. Recent studies have employed advanced analytical techniques (AFM, confocal microscopy and depth profiling)[107] in addition to conventional mechanical tests[89] to detect early signs of failure and to understand the mechanisms involved. Arrhenius-type models have been investigated for the purpose of predicting their service life.[45, 63]

The components of a 6-layered solar PV module (**Fig. 7**) typically include several plastic components and the useful lifetime of the modules is determined by their individual durability.[134] Failure in the field and in laboratory weathering studies are generally the result of degradation by solar UV radiation and micro-cracking of the plastic components, the encapsulants,[88, 134] back sheet,[107] and the polymer-based adhesives holding the module components together.[9, 107, 116] Back sheets serve to electrically insulate the cell and to protect other components from weathering by solar UV radiation. Encapsulants provide optical coupling of components and protect them from weathering and are commonly made of ethylene-vinyl acetate (EVA) co-polymer. In field observations, the back sheet and encapsulant were found to fail 9 and 4% of the time, respectively.[121] Back sheets made of poly(vinylidene difluoride), (PVDF) and poly(ethylene terephthalate) (PET) plastics were particularly susceptible to failure due to weathering, and accounted for 58 and 30% of the failed component in solar PV fields in China.[20] For instance, ~50% of the PVDF back sheets underwent yellowing within the first 5 years of use. Based on data available to date, poly(vinyl fluoride) [PVF] plastic appears to show some promise as a durable back sheet material but still needs long-term validation in the field.[71] Even better plastic formulations for the component applications need to be developed to ensure that modules survive their full functional lifetime.

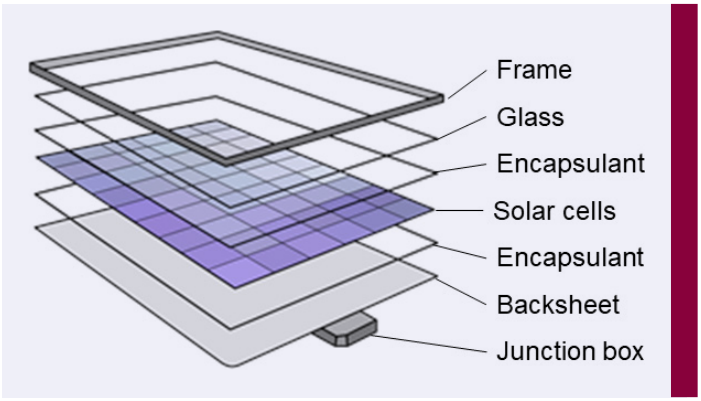

Fig. 7 **Exploded view of a solar PV module. Courtesy of Dow Chemical Company.**

With the new-generation organic PV devices, the light-sensitive layer itself is composed of polymers. The mechanisms of photodegradation of these photo-active polymer layers[14, 49, 101, 143, 155] as well as the durability of their plastic encapsulants in organic PV devices[10, 109] have been investigated. The residual additives in the light-sensitive polymer sandwiched between plastic laminates, were shown to promote accelerated degradation of these polymers.[173] Efforts at complete removal of trace additives prior to sealing the laminates during fabrication may help avoid this complication and extend their service life. Novel self-healing plastics also have been investigated recently to address the same problem of weather-induced cracking of encapsulants.[12] These smart-polymers are able to detect and

correct cracking thereby 'healing' the damage autonomously. The healing agent, such as a cyanoacrylate glue, is microencapsulated and dispersed in the plastic matrix. Microcracking of the matrix invariably ruptures microcapsules, releasing the healing agent that repairs the crack and prevents its further propagation. Modules with self-healing polymers performed well in laboratory weathering tests, losing only 15% of their power conversion efficiency under exposure conditions, whereas the untreated modules suffered a 90% deterioration of their efficiency in initial laboratory-accelerated weathering tests. An alternative strategy to stabilise the encapsulants in PV modules is the use of inorganic UV-absorbers in the formulation.[172] These need to be further developed and evaluated in field studies before they can be used in large-scale photovoltaic modules.

7 UV radiation and microplastics

Microplastics are loosely defined as plastic litter that is < 5 mm in size and includes primary and secondary microplastics. Primary microplastics are products that are manufactured as micro- or nano-scale materials. Facial creams and toothpaste contain microbeads in their formulations[40] and these routinely enter the wastewater stream and potentially end up in rivers and in oceans.[103, 175] More frequently encountered in the marine environment are the secondary microplastics; these are the meso- and micro-scale particles that are formed by fragmentation of larger plastic litter items during outdoor weathering.[7] Exposure of plastic litter to solar UV radiation is the critical first step that generates secondary microplastics from plastic debris. Macrofragmentation of weathered, embrittled plastics is commonly observed; however, recent data suggest that most of these microplastics are formed via the fracture of a highly-degraded surface layer of the plastics as opposed to progressive fractionation of plastic debris into daughter fragments[7] (**Fig. 8**). Surface embrittlement of plastic debris items following extensive oxidative degradation on exposure to solar radiation creates micro- and nano-particles that are released to the environment by mild abrasion of the surface due to wave or wind action.[7]

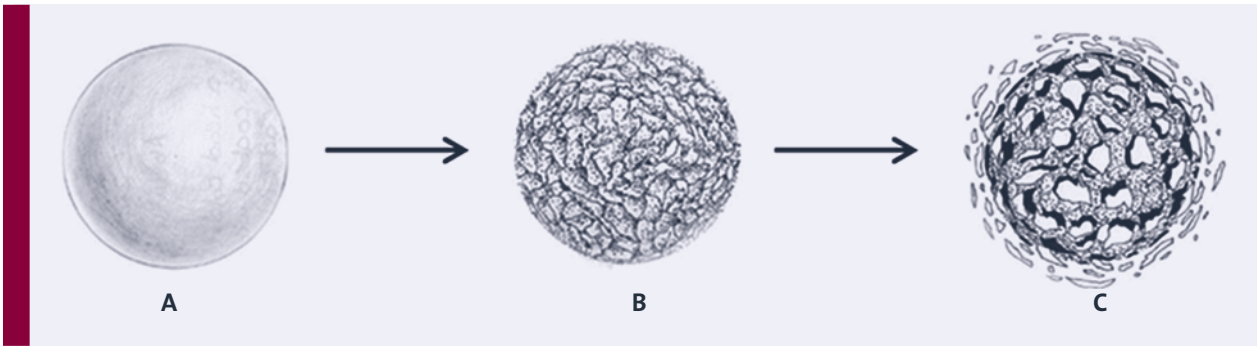

Fig. 8 **An artist's rendition of the surface ablation of fragmentation leading to microplastics and nanoplastics by weathering: (A) plastic bead, (B) surface embrittlement of bead due to solar UV-facilitated degradation, (C) ablation of surface into microplastics and nanoplastics.**

Bodies of freshwater[91, 103] and the oceans[28, 97, 144, 165] are well known to be contaminated with microplastics. Plastic materials absorb hydrophobic pollutants present in trace amounts in sea water and accumulate these at high concentrations. The ratio of the concentration of sorbed chemical in plastic suspended in water to its concentration in the water, is quantified by an equilibrium distribution constant K. Values of K are dependent on the properties of the

plastic as well as the chemical of interest but generally lie in the range of K~ 10^3–10^5 for most persistent organic pollutants (POPs) found in seawater. Marine organisms,[17, 147] especially fish[8, 82, 128, 153] routinely ingest the POP-contaminated microplastics. This creates a possible pathway for these chemicals to enter the marine food web.[86, 176] However, these organisms are also exposed to POPs via ingestion of lipid-rich prey. What fraction of the absorbed POPs in the microplastic might be bioavailable to the ingesting organism depends on the species and factors such as the stomach contents and residence time. The smaller the particle size of the plastic debris, the larger will be the group of marine animals able to ingest the particle (see Chapter 4). Data on adverse physiological impacts of such ingestion on a range of marine organisms are becoming increasingly available.[132, 186] While data on physiological impacts on ingesting organisms are size- and species-dependent,[22] laboratory exposure of fish larvae to micro- and nanoplastics show adverse effects at the behavioural and tissue/organelle level.[141] However, the dosages used in most studies appear to be much higher than those that might be reasonably expected in the environment. Nanoscale plastic particles are very likely also produced through the weathering degradation of microplastics. Although not observed as yet in either marine or freshwater environments, there is growing consensus that nanoplastics do occur in the oceans and that they are relatively more hazardous compared to microplastics.[16, 37]

Three key studies on the generation of microplastics that support the surface-ablation model (**Fig. 8**) were recently published. In one of these, the onset of fragmentation for HDPE plastic shopping bags exposed outdoors to solar radiation was established.[80] Although the fragmentation model in **Fig. 8** has been proposed as the main route to secondary microplastics, based on theoretical considerations,[7] this is the first instance where outdoor exposure of a plastic laminate was demonstrated to show such fragmentation. HDPE film samples of 0.1 mm thick exposed for 6 months on sand outdoors, completely disintegrated into microplastics (< 100 μm), while those exposed floating in seawater showed no significant fragmentation (but it is difficult to assess fragmentation in samples covered with foulants after exposures to seawater). The study[80] shows the critical role played by solar UV radiation in combination with high temperatures in the generation of microplastics. It also underlines the importance of beach clean-up in controlling generation of microplastics.

In a second study, nanoparticle-tracking analysis was used to measure nanoparticle formation when a polystyrene (PS) lid (used with coffee cups) was immersed in water and exposed to UV-visible radiation for 56 days at 32°C. It yielded 1.26 particles mL^{-1} compared to only 0.41 particles mL^{-1} for control, unexposed samples. Particle sizes were in the range of 0 to 2 μm.[99] Brine shrimp exposed to nanoscale PS particles show reduced feeding and abnormal multiple molting,[16] indicating leaching of toxic compounds by the weathered plastic. Nanoplastics that enter zebrafish larvae are known to relocate to specific organs in high concentrations.[141] The rapid fragmentation process occurs in coastal sediment as well. In a third study, polymer ropes made of PE, PP, and nylon exposed to coastal marine sediment at a depth of 10 m lost 0.39–1.02% of their mass per month.[185] However, loss of weight is generally an unreliable measure of degradation, especially in field studies.

8 Conclusions and gaps in knowledge

This assessment has highlighted recent advances in knowledge on solar UV-induced degradation of materials that allow for a better appreciation of the chemistry involved that would support the development of more effective stabilisers for materials. However, there

are some clear gaps in knowledge that need to be addressed for a better understanding of the issues discussed. These gaps are identified below.

- While activation and action spectra for yellowing and loss of strength are reported in the literature for base resins of common polymers, those for practical formulations of these plastics that contain additives and UV stabiliser are scarce. There is a need to generate wavelength sensitivity information for photo-damage of these materials.
- Material degradation, induced by solar UV-B radiation, is enhanced by the presence of other climate change factors, such as moisture, temperature, and air pollutants. Studies are needed to understand and quantify the synergetic effect of these parameters acting in concert on materials.
- Plastics used in packaging and building were hitherto selected and optimised based on durability and performance. The present focus on increased sustainability, especially the trend towards environmentally-sustainable buildings, requires such choices to be environmentally acceptable as well. A reassessment to develop novel, safer, effective and sustainable additives (colourants, plasticisers, and stabilisers) for plastic materials and wood coatings is needed. For instance, some of the plant-based additives (e.g., wood-derived lignin and heartwood extractives) appear to be effective UV stabilisers as well as environmentally sustainable. Particularly, in the current climate change scenarios, the utility of these as replacements for conventional synthetic stabilisers needs to be explored.
- Several nanoscale fillers have shown promise as stabilisers against solar UV-induced degradation of wood and plastics. However, their UV stabilisation properties appear to be limited to specific nanofiller-polymer combinations; the technical criteria to identify these combinations need to be worked out. Also, the economic feasibility of using these together with environmental concerns associated with potential leaching of nanomaterials from nanocomposite products during their use, need to be clarified.
- Heat treatment of wood is an environmentally sustainable method to enhance its dimensional stability and decay resistance. However, there are contradictory reports about the wood's resistance to UV radiation. Presence of heartwood extractives may influence the process. Therefore, more research is needed to clarify this (species dependence and/or extractives dependence).
- Solar energy is expected to fulfill a significant part of the future energy demand. The present solar modules have active-layer technologies that should last for 20 years or more in the field. The plastic envelope and other plastic components of the solar module fail prematurely in the field, because of solar UV-facilitated degradation. Increased UV radiation will contribute to an even shorter service of these modules. Research efforts on better stabilisation of these components using UV stabilisers and material substitution need more attention.

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Abbreviations and glossary

Abbreviation	Complete term
OH	Hydroxyl radical (an important atmospheric cleaning agent)
$1,25(OH)_2D$	1,25-dihydroxyvitamin D is the physiologically active form of *vitamin D*. It is formed primarily in the kidney by enzymatic hydroxylation of *25*-hydroxyvitamin D.
25(OH)D	25-hydroxyvitamin D is the major circulating form of vitamin D, the concentration of which in the blood is considered the best indicator of vitamin D supply to the body from cutaneous synthesis and nutritional intake.
AAPC	Average annual percentage change, when referring to the incidence of disease or sypmtoms.
AFM	Atomic force microscopy is a technique for analyzing the surface of a rigid material all the way down to the level of the atom. AFM uses a mechanical probe to magnify surface features up to 100,000,000 times, and it produces 3-D images of the surface.
Airshed	Airshed, an area where the movement of air (and, therefore, air pollutants) can be hindered by local geographical features such as mountains.
AK	Actinic keratosis, a rough, scaly patch on your skin that develops from years of exposure to the sun. It's most commonly found on your face, lips, ears, back of your hands, forearms, scalp or neck.
AMD	Age-related macular degeneration, a condition that results in blurred or no vision in the center of the visual field.
AMP	Anti-microbial peptide
ANSI	American National Standards Institute
AO	Arctic Oscillation. A large-scale variation in Arctic wind patterns
AOD	Aerosol Optical Depth is the sum of the absorption optical depth, which quantifies the attenuation of the direct solar beam due to absorption of photons and the scattering by aerosols.
APase	Alkaline phosphatase is an enzyme that liberates phosphate under alkaline conditions and is made in liver, bone, and other tissues.
APC	Antigen presenting cell is a type of immune cell that enables a T-lymphocyte (T-cell) to recognise an antigen and mount an immune response against the antigen. Antigen-presenting cells (APCs) include macrophages, dendritic cells, and B lymphocytes (B cells).
ASL	Above sea level
ATR	Attenuated total reflection is a sampling technique used in conjunction with infrared spectroscopy which enables samples to be examined directly in the solid or liquid state without further preparation.
Bayesian	Bayesian, usually referring to statistics, is based on the Bayesian interpretation of probability where this expresses a degree of belief in an event. The degree of belief may be based on prior knowledge about the event, such as the results of previous experiments, or on personal beliefs about the event. This differs from a number of other interpretations of probability.
BCC	Basal cell carcinoma(s) is the most common type of skin cancer. It often appears as a painless raised area of skin, which may be shiny with small blood vessels running over it; or it may present as a raised area with ulceration.

Abbreviation	Complete term
BDC	Brewer-Dobson Circulation, describes a pattern of atmospheric circulation according to which tropospheric air enters the stratosphere in the tropics and then moves upward and poleward before descending in the middle and high latitudes. It explains why tropical air has less ozone than polar air, even though most atmospheric ozone is produced in the tropical stratosphere.
Br	Bromine (an ozone depleting chemical)
BRAF	B-Rapidly Accelerated Fibrosarcoma, a gene that is commonly mutated in melanoma
BrO	Bromine monoxide
Browning	Decreases in the transparency of inland and coastal waters due to increases in terrestrially-derived organic matter.
BSWF	Biological spectral weighting functions
BWF	Biological weighting function
CAS	Chemical Abstracts Service
CAT	Catalase, An enzyme found in most living cells that catalyzes the decomposition of hydrogen peroxide to water and oxygen
CC	Cortical cataract(s) are found in the lens of the eye and are characterised by white, wedge-like opacities that start in the periphery of the lens and work their way to the center in a spoke-like fashion.
CCl_4	Carbon tetrachloride (an ozone depleting gas)
CCM	Chemistry-climate model (used to predict future changes in atmospheric composition)
CCMI	the Chemistry-Climate Model Initiative
CDK	Climatic droplet keratopathy is a degenerative condition characterised by the accumulation of translucent material in the eye. It begins peripherally and spreads centrally. Progressive accumulation in later life can lead to significant visual disability, and people leading an outdoor life are particularly at risk.
CDK4	Cyclin-dependent kinase 4; mutations in the gene are found in melanoma
CDKN2A	Cyclin-dependent kinase inhibitor 2A; a gene commonly mutated in melanoma
CDOC	Coloured dissolved organic carbon (see CDOM)
CDOM	Coloured (or chromophoric) dissolved organic matter is the humic-rich, optically active fraction of dissolved organic matter that is present in natural waters from the decomposition of detritus and other organic material.
CDR	Carbon dioxide reduction is the conversion of carbon dioxide to more reduced chemical species using energy, such as electricity.
Centile	A centile is the value equivalent to one hundredth of a range of values in cumulative frequency distribution.
CeO_2	Cerium oxide
CFC	Chlorofluorocarbon. Ozone depleting substance (e.g., $CFC1_2$: dichlorodifluoromethane, CCl_2F_2), now controlled under the Montreal Protocol.

Abbreviation	Complete term
CH	Contact hypersensitivity is a form of delayed-type or cell-mediated hypersensitivity expressed in the skin. It is initiated by agents/antigens that penetrate through the stratum corneum into the epidermis. Once the immune system has been activated, topical re-exposure to the relevant antigen elicits an inflammatory response, characterised by delayed formation of edema.
CH_4	Methane (a greenhouse gas)
$CHCl_3$	Chloroform (an ozone depleting gas)
CI	Confidence interval is an interval that will contain a population parameter a specified proportion of the time, 95% in most common use of this term.
CIE	*Commission Internationale de l'Eclairage* (International Commission on Illumination)
Cl	Chlorine (an ozone depleting gas)
CMF	Cloud modification Factor
CMIP5	Fifth Coupled Model Intercomparison Project
CMM	Cutaneous malignant melanoma is a malignancy of pigment-producing cells (melanocytes) located predominantly in the skin, but also found in the eyes, ears, GI tract, mucous membranes.
CNT	Carbon nanotubes are forms of carbon with a cylindrical nanostructure. These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology.
CO	Carbon monoxide, a gas found in the atmosphere.
CO_2	Carbon dioxide (a greenhouse gas)
COS	Carbonyl sulfide
COT	Cloud optical thickness
CPD	Cyclobutane pyrimidine dimer(s) are molecules formed from thymine or cytosine bases in DNA via photochemical reactions from exposure to UV radiation and are indicators of genetic damage.
CPE	Chlorinated polyethylene, a form of plastic.
CPVC	Chlorinated Poly Vinyl Chloride is a thermoplastic produced by chlorination of polyvinyl chloride (PVC) resin, which is significantly more flexible and can withstand higher temperatures than standard PVC.
CR	Chlorinated rubber is a nonrubbery, incombustible rubber derivative produced by the action of chlorine on rubber in solution. It is used in corrosion-resistant paints and varnishes, and in inks and adhesives
Cu	Copper (Cu(I) and Cu(II) being different oxidation states)
de minimis	Something, such as a risk, that in lacking significance or importance, and is so minor as to merit being disregarded.
DIC	Dissolved inorganic carbon
DMS	Dimethylsulfide
DMSP	Dimethylsulfoniopropionate

Abbreviation	Complete term
DNA	Deoxyribonucleic acid
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DON	Dissolved organic nitrogen
DSB	Double strand break occurs when both strands of DNA break and, if unrepaired, the resulting chromosome discontinuity often results in death of the cell.
DSCOVR	Deep Space Climate Observatory
DTH	Delayed type hypersensitivity
DU	Dobson unit (used for the measurement of total column ozone ($1\ DU = 2.69 \times 10^{16}$ molecule cm^{-2})
DVM	Daily vertical migration
EAE	Experimental allergic encephalitis is the most commonly used experimental model for the human inflammatory demyelinating disease, multiple sclerosis.
EDUCE	European Database for Ultraviolet Radiation Climatology and Evaluation
EESC	Equivalent Effective Stratospheric Chlorine. A term used to represent the total chlorine concentration in the stratosphere from all sources of ozone depleting substances (including CFCs, HCl, Cl_2, $ClONO_2$, etc) and a scaled contribution from other halocarbons and bromine, taking its ODP into account.
ENSO	El Niño Southern Oscillation, a large-scale climate variability in the Pacific region.
EP	Earth Probe (a NASA satellite)
EPA	Environmental Protection Agency
EPDM	Ethylene propylene diene is a synthetic polymer with rubber-like properties and good resistance to environmental exposure.
EV	*Epidermodysplasia verruciformis* is a rare, heritable disease characterised by an unusual susceptibility to infection with specific types of human papillomavirus and a propensity for developing malignant skin tumours.
EVA	Ethylene-vinyl acetate is the copolymer of ethylene and vinyl acetate. It's an extremely elastic material that can be sintered to form a porous material that is like rubber.
Fe	Iron (Fe(II) and Fe(III) being different oxidation states)
FMI	Finnish Meteorological Institute
Folliculogenesis	Folliculogenesis is the maturation of the ovarian follicle, a densely packed shell of cells that contains an immature egg cell. It occurs as part during the menstrual cycle.
FTIR	Fourier transform infrared is an analytical technique used to identify organic materials. This technique measures the absorption of infrared radiation by the sample material versus wavelength. The infrared absorption bands identify molecular components and structures.
GDP	Gross domestic product

Abbreviation	Complete term
GEM	Gaseous elemental mercury, mercury in the form of a vapour.
GHG	Greenhouse gas
Glu I	A pathogenesis-related (PR) protein
GNA11	Guanine nucleotide-binding protein subunit alpha-11, a gene coding for proteins involved in various transmembrane signaling systems.
GNAQs	Guanine nucleotide-binding proteins G(q) are a family of proteins that act as molecular switches inside cells. They are involved in transmitting signals from a variety of stimuli outside a cell to its interior.
GOME	Global Ozone Monitoring Experiment
GPC	Gel permeation chromatography is that separates analytes on the basis of the size of the molecules.
GRP	Glass-reinforced polyester is composite material made of a plastic matrix reinforced with fibres of glass.
GST	Glutathione-S-transferase is a metabolic best known for its ability to catalyze the conjugation of the reduced form of glutathione (GSH) to xenobiotic substrates for the purpose of detoxification.
GWP	Global warming potential. A measure of the warming effectiveness of a gas compared with CO_2
H_2O_2	Hydrogen peroxide
Hadley cell or circulation	A large-scale atmospheric convection cell in which air rises at the equator and sinks at medium latitudes, typically at about 30° northern or southern latitudes.
Haemorrhagic stroke	Hemorrhagic is as medical condition that results from the rupture of a blood-vessel in the brain.
HALS	Hindered Amine Light Stabilizers are chemical compounds containing an amine functional group that are used as stabilizers in plastics and polymers for protection against UV radiation.
HCFC	Hydrochlorofluorocarbon. Interim replacements for CFCs with small ozone depletion potential (e.g., R22: chlorodifluoromethane $CHClF_2$) to be phased out.
HDPE	High-density polyethylene is a a class of polyethylene.
HFC	Hydrofluorocarbon replacements for CFCs
HFO	Hydrofluoroolefine, replacements for CFCs and HFCs, and HCFCs. An example is 2,3,3,3 tetrafluoropropene (HFO-1234-yf).
Hg	Mercury (Hg(0) and Hg(II) being different oxidation states)
HIV	Human immunodeficiency virus
HNV	Hematopoietic necrosis virus is an RNA virus that causes the disease known as infectious hematopoietic necrosis in salmonid fish such as trout and salmon.
HONO	Nitrous acid
HPV	Human papillomavirus

Abbreviation	Complete term
HR	Hazard ratio is the ratio between the responses observed in the exposed and control groups in an epidemiological study.
HSV	*Herpes simplex* virus
HY5	Transcription factor HY5, which is a key downstream effector of the UVR8 (UV-regulatory protein) pathway in plants.
Hypertension	Also known as high blood pressure, hypertension is a chronic medical condition in which the blood pressure in the arteries is persistently elevated. High blood pressure usually does not cause symptoms but is associated with increased risk of heart attack and stroke.
IBD	Inflammatory bowel disease
Ig	Immunoglobulin
IL	Interleukin
Ink4a	Murine inhibitor of kinase 4a protein (gene in italics)
Interquartile range	The interquartile range [IRQ] is a measure of statistical dispersion and is equal to the difference between 75th and 25th centiles, or range of data between upper and lower quartiles.
IPCC	Intergovernmental Panel on Climate Change
IPF	Immune protection factor
Ischaemic stroke	Ischemic stroke is a medical condition that results of an obstruction (a blood clot) within a blood vessel supplying blood to the brain.
KC	Keratinocyte cancers. Formerly called non-melanoma skin cancers and including squamous cell and basal cell carcinoma (SCC and BCC, respectively).
Kaposi sarcoma	Kaposi sarcoma is a rare tumor that has numerous types, the most common of which is associated with advanced HIV. All forms of Kaposi sarcoma (KS) are caused by a type of herpesvirus, Kaposi sarcoma herpesvirus (KSHV). Most people with KSHV do not develop Kaposi sarcoma unless their immune system is suppressed
kda	Kilodalton
KNMI	Dutch National Institute for Weather, Climate and Seismology (Netherlands)
LCA	Lifecycle analysis is a technique to assess environmental impacts associated with all the stages of the life of a product from extraction of raw material through processing, manufacture, distribution, use, repair and maintenance, and disposal or recycling.
Lentigo maligna melanoma	Lentigo maligna melanoma is a type of invasive skin cancer. It develops from lentigo maligna, which is sometimes called Hutchinson's melanotic freckle. Lentigo maligna stays on the outer surface of the skin. When it starts growing beneath the skin's surface, it becomes lentigo maligna melanoma.
LDPE	Low-density polyethylene is a class of polyethylene.
LER	Lambertian equivalent reflectivity
LLDPE	Linear low-density polyethylene is a class of polyethylene that is used in the manufacture of flexible products including thin-gauge plastic film.

Abbreviation	Complete term
MAAs	Mycosporine-like amino acids, compounds that protect organisms from UV damage through their absorption of UV as well as their antioxidant capacity.
Mb	Megabase, equal to 1 million base pairs of DNA
MC1R	Melanocortin 1 receptor, a gene coding for proteins involved in regulating colour of mammalian skin and hair.
MDD	Minimal vitamin-D dose
MED	Minimal erythema dose
MCC	Merkel cell carcinoma is a rare, highly aggressive, skin cancer mainly affecting the elderly and the immunosuppressed.
Meta-analysis	A *meta-analysis* is an analysis that uses a statistical approach to combine the results from multiple studies to increase power (over individual studies), improve estimates of the size of the effect, and/or to resolve uncertainty when individual reports are inconsistent or present different findings.
MHC	Major histocompatibility complex is a genetic system that allows large proteins in the cells of the immune system to identify compatible or foreign proteins. It allows the matching of potential organ or bone marrow donors with recipients.
Mixed Layer Depth	The depth to which surface waters of inland or oceanic waters mix freely due to uniform temperature and wind-driven mixing.
Mineralization	Mineralization (referring to soil) is the decomposition, i. e. oxidation of organic matter into small molecules such as carbon dioxide, water, and ammonia.
MMT	Million metric tons
MP	Micro-plastics are small pieces of plastic less than five millimeters long.
MS	Multiple sclerosis is a chronic, typically progressive disease involving damage to the sheaths of nerve cells in the brain and spinal cord. Symptoms include numbness, impairment of speech and of muscular coordination, blurred vision, and severe fatigue.
mtDNA	Mitochondrial DNA is DNA found in the mitochondria of the cell.
Myocardial infarction	Acute myocardial infarction is the medical name for a heart attack. A heart attack is a life-threatening condition that occurs when flow of blood to the heart muscle is abruptly cut off, causing tissue damage. This is usually the result of a blockage in one or more of the coronary arteries.
N_2O	Nitrous oxide (a greenhouse gas that is also a source of NO_2)
NAO	North Atlantic Oscillation. A large-scale variation and redistribution of atmospheric mass in the Atlantic region producing large changes in the Northern hemisphere dynamics.
NASA	National Aeronautics and Space Administration (USA).
NaTFA	Sodium trifluoroacetate, the sodium salt of trifluoroacetic acid.
NC	Nuclear cataract(s) are the most common type of age-related cataract, caused primarily by the hardening and yellowing of the central portion of the lens of the eye over time.
NCAR	National Centre for Atmospheric Research, USA
NH	Northern Hemisphere

Abbreviation	Complete term
NIMBUS-7	A NASA satellite
NIVR	Netherlands Agency for Aerospace Programmes
NMHCs	Non-methane hydrocarbons
NMSC	Non-melanoma skin cancer
NO	Nitric oxide (an ozone depleting gas)
NO_2	Nitrogen dioxide (an ozone depleting gas)
NOAA	National Oceanic and Atmospheric Administration, USA
NOAEL	No observed adverse effect level, a level of exposure below which no adverse effects are observed in a test organism, similar to NOAEC.
NOEC	No observed effect concentration, a concentration of exposure below which no effects of any kind are observed in a test organism.
NOEL	No observed effect level, a level of exposure below which no effects of any kind are observed in a test organism, similar to NOEC.
NOM	Natural organic matter including particulate organic matter (POM) and dissolved organic matter (DOM).
NOX	Nitrogen oxides
NP	Nanoparticle
O_3	Ozone
OA	Organic aerosols
OCA	Oculocutaneous albinism is a group of rare inherited disorders characterised by a reduction or complete lack of melanin pigment in the skin, hair, and eyes. These conditions are caused by mutations in specific genes that are necessary to produce melanin pigment in specialised cells in the skin, called melanocytes.
OCS	Carbonyl sulfide
ODP	Ozone depletion potential. The ratio of the impact on ozone of a chemical compared to the impact of a similar mass of CFC-11. Thus, the ODP of CFC-11 is defined to be 1.0.
ODS	Ozone depleting substance(s) such as the CFCs
OMI	Ozone Monitoring Instrument (on board the Aura satellite)
OMZs	Oxygen minimum zones, i.e. zones in marine systems with low oxygen concentration
OR	Odds ratio; odds that an outcome will occur given an exposure to a chemical, as disease, or an environmental condition, compared to the odds of the outcome occurring in the absence of that exposure.
OTR	Organ transplant recipients
P	Phosphorous
PAH	Polycyclic Aromatic Hydrocarbon
PAM	Pulse amplitude modulated (fluorescence), a measure of the efficiency of photosynthesis

Abbreviation	Complete term
PAR	Photosynthetically Active Radiation, 400–700 nm waveband
PAUR II	Photochemical Activity and solar Ultraviolet Radiation campaign 2
PB	Polybutene is a liquid oligomer widely used as a plasticisers for high-molecular weight polymers, such as polyethylene, and as carriers and lubricants. They are not to be confused with the high molecular weight polymer polybutene.
PB-1	Polybutylene is a high molecular weight, linear, and semi-crystalline polymer.
pCO_2	Partial pressure of carbon dioxide
PE	Polyethylene is is a major class of thermoplastic polymers, produced by the polymerization of ethylene. Depending on the polymerization process used, various types of polyethylene with differing properties can be obtained.
PEC	Predicted environmental concentration
PER	Photoenzymatic repair
PET	Poly(ethylene terephthalate) is a thermoplastic material commonly used in the form of fibres, films, and as containers for food and beverages.
PFBI	Perfluoro-n-butyl iodide, a substitute for CFCs used as a solvent for cleaning during the maintenance of aircraft.
Pg	Peta gram (1x1012 grams)
Photoageing	Photoaging is premature aging of the skin caused by repeated exposure to ultraviolet radiation, primarily from the sun but also from artificial sources.
Photoreact(ion)	Generally used to describe a chemical reaction caused by absorption of ultraviolet, visible or infrared radiation. Synonym for “photochemical reaction”.
Photofacilitation	A process whereby UV radiation interacts with organic matter to make it more easily consumed by microbes and fungi in the environment.
Photodermatoses	Photodermatoses are a group of cutaneous disorders characterised by an abnormal reaction to exposure to light.
Photo-dissolution	A photochemical reaction that results in the substance becoming more soluble in water.
Photosensitiser	A photosensitiser is a molecule that produces a reactive transient species including reactive oxygen species (ROS) in photochemical reactions. Reactive transient species react with another molecule, e.g., a contaminant or DNA and RNA.
PHR1	The gene encoding CPD photolyase
Phycobilins	Pigments that absorb light for photosynthesis in cyanobacteria and some other algae.
PI	A prediction interval [PI] is a range of values in which future observations will fall, with a certain probability, given what has already been observed.
PLA	Polylactic acid is biodegradable plastic derived from renewable resources, such as corn starch.
PLE	Polymorphic light eruption is a skin rash triggered by exposure to sunlight or artificial ultraviolet (UV) radiation.
PM	Particulate matter (aerosols in the atmosphere)

Abbreviation	Complete term
PM_{10}	Particulate matter in air that is smaller than 10 µm.
$PM_{2.5}$	Particulate matter in air that is smaller than 2.5 µm and is inhaled deeper into lungs than larger particles (PM_{10}).
PMMA	Polymethyl methacrylate is a glassy synthetic plastic used to make products such as Perspex®, Plexiglas®, and Lucite®
PNEC	Predicted no effect concentration is a concentration of a substance that is predicted to not cause any effects in organisms exposed to it.
POC	Particulate organic carbon
POM	Particulate organic matter
POP(s)	Persistent organic pollutants are chemicals of global concern due to their potential for long-range transport, persistence in the environment, ability to bio-magnify and bio-accumulate in ecosystems, as well as their significant negative effects on human health and the environment.
Porphyrias	The porphyrias are a group of conditions in which chemicals (porphyrins) are abnormally increased in the body.
PP	Polypropylene is a type of plastic used for many purposes, such as food packaging, making ropes, and making artificial fabrics.
ppm (ppb)	Parts per million. A mixing ratio of 1 molecule of a substance per million molecules of air. Similarly, ppb is parts per billion, one molecule per billion molecules of air.
PR	Pathogenesis-related proteins
Prospective study	A prospective study is an epidemiological study which follows disease incidence in a cohort of individuals over time.
PS	Polusulphone, a thermoplastic that contains sulfur and is resistant to high temperatures.
PS	Polystyrene is a plastic typically used for containers and also as a stiff foam for containers but also as insulation in buildings, refrigerators, and air conditioners.
PSC	Posterior subcapsular cataract(s) is a cataract begins as a small opaque or cloudy area on the “posterior,” or back surface of the lens of the eye.
PSC	Polar stratospheric cloud (ice crystals which form at high altitudes in Polar regions when the temperature is below a critical threshold)
PSI	Photosystem I is a multi-subunit protein complex located in the membranes of green plants and algae. It initiates one of the first steps of conversion of solar energy to chemical energy by light-driven transport of electrons.
PSII	Photosystem II is a membrane protein super-complex that executes the initial reaction of photosynthesis in higher plants, algae, and cyanobacteria.
Ptc	Murine patch protein (gene written in italics, *Ptc*)
PTCH	Human patch protein (gene written in italics, *PTCH*)
PV	Photovoltaic, referring to the conversion of light into electrical energy.
PVC	Poly(vinyl chloride) a solid polymer made from vinyl chloride. PVC is used to make pipes, vinyl flooring and siding, hoses, cable coatings, medical devices, and plumbing and automotive parts.

Abbreviation	Complete term
PVDF	Poly(vinylidene difluoride) is non-reactive thermoplastic fluoropolymer produced by the polymerization of vinylidene difluoride. PVDF is a specialty plastic used in applications requiring resistance to solvents, acids and bases,
PVF	Poly(vinyl fluoride) is is a thermoplastic fluoropolymer that is structurally similar to polyvinyl chloride. PVF has low permeability for vapors, burns very slowly, and has excellent resistance to weathering and staining. It is also resistant to most chemicals.
QBO	Quasi Biennial Oscillation, a shift in wind patterns – especially over the tropics – with a period of approximately 2.2 years.
OSSN	Ocular Surface Squamous Neoplasia, an uncommon cancer of the surface of the eyeball.
Quintile	Any of the four values that divide the items of a frequency distribution into five classes with each containing one fifth of the total population. The upper quintile of a data-set includes the values falling between 80 and 100% in cumulative frequency distribution.
RA	Rheumatoid arthritis
RAC1	Ras-related C3 botulinum toxin substrate (gene in italics); mutations of the gene are found in melanoma.
Radiative Forcing	A measure of the influence a factor (e.g., GHGs, ice albedo, tropospheric aerosols, etc.) has in altering the balance of incoming solar and outgoing infrared irradiance (W m^{-2}) in the Earth-atmosphere system. It is an index of the importance of the factor as a potential climate change mechanism. Radiative forcing is approximately proportional to temperature changes at Earth's surface, so a positive radiative forcing is associated with heating in the troposphere.
RAF	Radiation amplification factor (a measure of sensitivity to change in ozone)
RCP	Representative Concentration Pathways: Scenarios for future climate resulting from different combinations of economic, technological, demographic, policy, and institutional futures, defined by their total radiative forcing. RCPs are greenhouse gas concentration (not emissions) trajectories adopted by the IPCC for its fifth Assessment Report (AR5) in 2014. The pathways are used for climate modelling and research. They describe four climate futures, which differ on how much greenhouse gases are emitted in years to come. The four RCPs, RCP 2.6, RCP 4.5, RCP 6, and RCP 8.5 are named after a possible range of radiative forcing values in the year 2100 relative to pre-industrial values (+2.6, +4.5, +6.0, and +8.5 W m^{-2}, respectively).
ROS	Reactive oxygen species are unstable molecules that contain oxygen and that easily react with other molecules. Reactive oxygen species in cells may cause damage to DNA, RNA, and proteins. Examples include peroxides, superoxide, hydroxyl radical, singlet oxygen, and alpha-oxygen.
RR	Relative risk, is ratio of the risk in the exposed compared to the risk in the non-exposed population.
RT	Radiative transfer, is the physical phenomenon of energy transfer in the form of electromagnetic radiation. The propagation of radiation through a medium is affected by absorption, emission, and scattering processes. The equation of radiative transfer describes these interactions mathematically.
SAGE	Stratospheric Aerosol and Gas Experiment, a satellite-based instrument

Abbreviation	Complete term
SAM	Southern Annular Mode, the north-south oscillation of the stream of westerly winds at middle to high latitudes in the Southern Hemisphere.
SCC	Squamous cell carcinoma
SCCC	Squamous cell carcinoma of the cornea and conjunctiva of the eye.
SCIAMACHY	Scanning Imaging Absorption Spectrometer for Atmospheric Chartography
SD (SE)	Standard Deviation, a measure of the variance of a range of values. Standard Error is a similar term used in statistics.
SED	Standard Erythemal Dose, equals 100 J m^{-2} of erythemally-weighted UV irradiance, which quantifies the effect of UV radiation in the development of sunburn.
SEM	Scanning electron microscopy
SEVIRI	Spinning Enhanced Visible and InfraRed Imager
SH	Southern hemisphere
SIR	Standardised incidence ratios, used to correct for differences in age and/or sex when comparing the incidence of a disease with that in the general population.
SOD	Superoxide dismutase
SODIS	Solar disinfection, the use of solar radiation to kill bacteria and inactivate viruses.
SOX	Oxides of sulfur
Spatio-temporal	Usually referring to an analysis or model that includes consideration of spatial and temporal characteristics of observations.
SPF	Sun Protection Factor, a measure of the ability of a sunscreen to protect against sunburn. Estimated by comparing the dose of erythemally weighted UV radiation required to cause sunburn with sunscreen applied to that with none applied.
SRM	Solar Radiation Management, is also known as geoengineering, which involves engineering solutions to reduce the amount of solar energy reaching the surface of the earth.
ssUV	Solar Simulated Ultra Violet
SSA	Single scattering albedo, quantifies the absorption efficiency of aerosols
SST	Sea Surface Temperature
STAT	Signal transducer and Activator of Transcription, a gene that regulates many aspects of growth, survival and differentiation in cells.
SZA	Solar Zenith Angle, the solar elevation angle from the horizontal measured in degrees.
TB	Tuberculosis, a disease of humans and some domestic and wild animal.
tDOM	Terrestrially-derived dissolved organic matter
TEMIS	Tropospheric Emission Monitoring Internet Service
TFA	Trifluoroacetic acid

Abbreviation	Complete term
Th1	T-helper cell 1, specific groups of immune cells defined by certain markers on their surface.
Th2	T-helper cell 2, specific groups of immune cells defined by certain markers on their surface.
Thermocline	The intermediate depths of inland or oceanic waters that show a rapid decline in temperature with increasing depth; sometimes also used to refer to the single depth of maximum temperature change with depth.
TiO_2	Titanium dioxide
TOC	Total ozone column, essentially the total amount of ozone between the upper stratosphere and the point of measurement.
TOMS	Total Ozone Mapping Spectrometer, a satellite-based instrument
Transient species	A short-lived intermediate in a chemical reaction
Treg cell	T-regulatory cells are a subpopulation of T cells that modulate the immune system and maintain tolerance to self-antigens.
Troposphere	Lowest part of the earth's atmosphere (0–16 km above sea level)
UCA	Urocanic acid
UML	Upper mixed layer, of water in lakes or the ocean
UNEP	United Nations Environment Programme
UPF	UV protection factor
UV	Ultraviolet. Wavelengths from 100 nm to 400 nm. Ozone and other atmospheric gases progressively absorb more and more of the radiation at wavelengths less than 320 nm. Only those greater than 290 nm are transmitted to the Earth's surface.
UV-A	Electromagnetic radiation of wavelengths in the 315 to 400 nm range (weakly absorbed by ozone)
UV-B	Electromagnetic radiation of wavelengths in the 280 to 315 nm range (strongly absorbed by ozone)
UV-C	Electromagnetic radiation of wavelengths in the 100 to 280 nm range (solar UV-C is not transmitted to Earth's surface)
UV_{eff}	UV irradiance weighted by the spectral sensitivity of an effect, integrated over wavelength.
UV_{ery}	Erythemally-weighted UV irradiance, where the irradiance is weighted by the erythemal action spectrum.
UVI	UV index. A measure of erythemally-weighted UV for providing information to the public. UVI values greater than 10 are considered "extreme" by the WHO. If UV_{ery} is specified in units of W m^{-2}, then UVI = 40 x UV_{ery}).
UVR	Ultraviolet radiation is electromagnetic radiation or light having a wavelength of 100 to 400 nm. See "UV".
UVR8	UV-regulatory protein
VDR	Vitamin D receptor
VOC	Volatile organic compound (s)

Abbreviation	Complete term
VSLS	Very short-lived (with tropospheric lifetimes less than 6 months) halogenated substances, i.e. naturally produced halogenated (mainly brominated) substances than can reach the stratosphere.
WHO	World Health Organization
WMO	World Meteorological Organization
WOUDC	World Ozone and UV Data Centre
WPC	Wood-plastic composites
XP	*Xeroderma pigmentosum*, recessive genetic disorder of DNA repair in which the ability to repair damage caused by UV radiation is compromised.
ZnO	Zinc oxide

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